University of Southampton Research Repository

Thesis: Elizabeth Sarah Marsden (2019) "The Role and Implications of Mineral Associations in Organic Carbon Preservation", University of Southampton, Faculty of Environmental and Life Sciences, School of Ocean and Earth Science PhD Thesis, pagination.

University of Southampton

Faculty of Environmental and Life Sciences

Ocean and Earth Science

The Role and Implications of Mineral Associations in Organic Carbon Preservation

DOI

by

Elizabeth Sarah Marsden

ORCID ID 0000-0002-4150-6636

Thesis for the degree of Doctor of Philosophy

December 2019

University of Southampton

Abstract

Faculty of Environmental and Life Sciences

Ocean and Earth Science

Thesis for the degree of Doctor of Philosophy

The Role and Implications of Mineral Associations in Organic Carbon Preservation

by

Elizabeth Sarah Marsden

Organic matter-mineral interactions are a key part of the global carbon cycle, facilitating the preservation of organic matter that helps remove CO_2 from the atmosphere and allow for the build-up of oxygen in the ocean-atmosphere system.

In this project, chemical standards were added to clay and iron minerals (kaolinite, bentonite and goethite), to investigate the effect of organic matter and mineral type on sorption, as well as investigating the mechanisms by which binding is occurring. Sorption was found to be greatest in aromatic compounds across all three minerals used. Different organic compounds showed a slight preference for different minerals, but overall mineral type had a minimal effect on bonding. Organic compounds were found to bind cooperatively, achieving a higher organic matter: mineral ratio than the monolayer equivalent often observed in sediments. This suggest that the observed monolayer equivalence in marine sediments may be due to the nature and quantity of organic matter reaching these sediments rather than an inherent limit on the amount of organic matter that mineral surfaces can sorb.

Experiments were also carried out using natural dissolved organic matter (DOM) under riverine and marine conditions to determine the impact of minerals on riverine DOM transport. The different DOM sources were found to have a minimal effect on the degree of sorption with salinity and mineral mass having the greatest effect. This observation suggests that much lower coverage was achieved for the DOM than for the standards, possibly due to the presence of a more limited range of compounds.

Differences between the dissolved and standards data highlight the importance of including all compound types in the study of organic matter-mineral interactions. Given the complex nature of these interactions, and the different factors effecting them, further work is need to fully understand the role they play in organic matter preservation. However, this work has demonstrated the importance of careful experimental design, and the inclusion of both dissolved and particulate matter.

Table of Contents

Table of Tables

Table of Figures

Research Thesis: Declaration of Authorship

Print name: Elizabeth Marsden

Title of thesis: The Role and Implications of Mineral Associations in Organic Carbon Preservation

I declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;
2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
3. Where I have consulted the published work of others, this is always clearly attributed;
4. Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
5. I have acknowledged all main sources of help;
6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
7. None of this work has been published before submission

Signature:

Date:

Acknowledgements

Firstly I would like to extend my gratitude to my supervisory team: Martin Palmer and Jessica Whiteside, as well as my panel chair Rachael James for their help, support and feedback throughout my PhD. I would also like to thank the organic geochemistry lab team: Sargent Bray, Megan Spencer and Bastian Hambach for teaching me new methods and trying to answer my experimental questions. Thanks also to the aquarium team: Robbie Robinson and Nicola Pratt for the use of equipment and algae; to Duncan Purdie and Cynthia Dumousseaud for the use of and training in Dissolved Organic Carbon measurements; to Richard Pearce and Ross Williams for carrying out the X-ray diffraction analysis and to Darren Bradshaw, India Willimott and Nikolay Zhelev for carrying out BET surface area measurements.

I am also grateful to my fellow organic geochemistry students, Sarah, Amy, Libby and Natasha for their inputs into a number of talks and posters as well as for making the lab a more interesting and entertaining place to be in. I was also made to feel very welcome during my visit to CEH Bangor and would like to thank all the staff there especially Ed Rowe who acted as my supervisor during the placement and Inma Robinson and Adam Pickard who helped me in the labs.

This thesis was supported by the Natural Environmental Research Council [grant number NE/L002531/1]’for the SPITFIRE DTP at University of Southampton. I am also grateful to Mary Smith who seemed to know the answer to every PhD related question you could think of.

Additionally, I would like to thank my officemates from 566/13 for their support and occasional distractions (including buying coral the office cat) as well as looking after my plants whenever I was away. On the topic of distraction, a mention must be made of the Student Scout and Guide Organisation which helped keep me sane, or at least no more insane than when I started, by providing fun and friendship completely outside of my PhD. And of course, many thanks to my friends and family for their continued support - especially to my parents for their proof reading services and to Oli for attempting to keep the balance between my PhD, Guiding and life in general.

Definitions and Abbreviations

BET	Brunauer-Emmett-Teller	Method of surface area measurement using gas (typically N2) sorption
BSTFA	N,O-bis(trimethylsilyl) trifluoroacetamide	
DCM	Dichloromethane	
DOC	Dissolved Organic Carbon	
DOM	Dissolved Organic Matter	That able to pass through a GF/F filter in Marine science and a GF/C filter in soil science
EA	Elemental Analysis	
EEM	Excitation Emission Matrix	
fDOM	Fluorescent Dissolved Organic Matter	
GC-MS	Gas Chromatography-Mass Spectrometry	
GF/C	Glass Fibre Filter Size C	Pore size of 0.45 µm
GF/F	Glass Fibre Filter Size F	Pore size of 0.7 µm
OM	Organic Matter	
POC	Particulate Organic Carbon	
SEC	Specific Electrical Conductivity	
TDN	Total Dissolved Nitrogen	
TEM	Transition Electron Microscopy	
TOC	Total Organic Carbon	
XPS	X-ray Photoelectron Spectroscopy	
XRD	X-ray Diffraction	

Chapter 1 Introduction

1.1 The global carbon cycle

The carbon cycle is the central geochemical driver of the Earth's climate system. The cycle describes the exchanges of carbon between the Earth's reservoirs (sinks) and sources (Allaby, 2008). On million-year time scales, feedbacks in the system stabilize Earth's climate and oxygen concentrations through silicate weathering. On hundred-thousand-year timescales, the carbon cycle in the ocean amplifies climate change. On human time scales of decades, the carbon cycle dampens climate change by absorbing fossil-fuel CO_2 into the oceans and land biosphere (Archer, 2010). Figure 1.1 (black lines) show how under natural conditions carbon dioxide produced by respiration, weathering and fires is balanced by that created during photosynthesis, however human activity has led to an upsetting of this balance (Figure 1.1 red lines) (Friedlingstein, 2015)

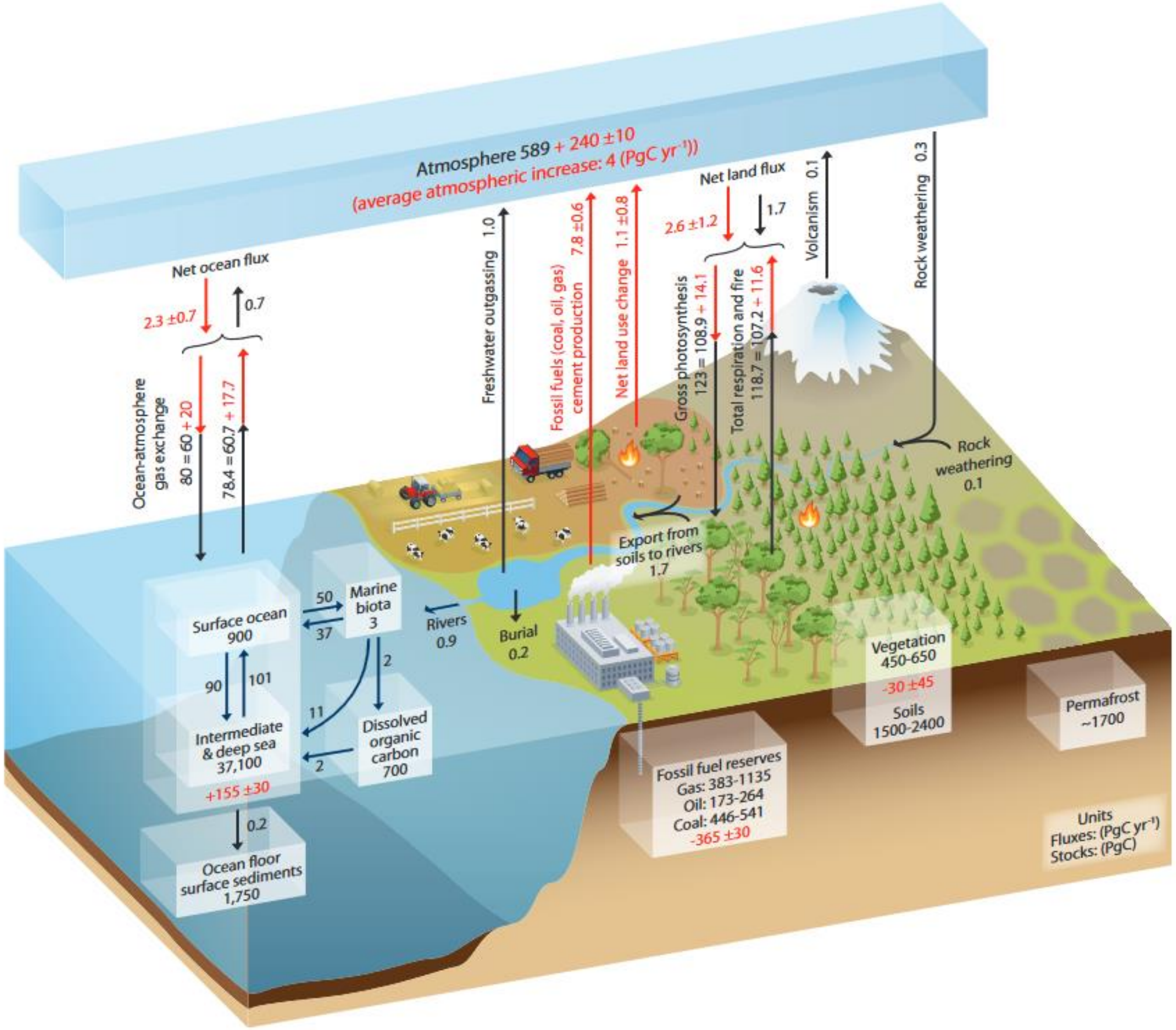


Figure 1.1. Schematic of the global carbon cycle showing the transfer of carbon through the Earth and life systems. Black numbers and arrows indicate reservoir mass and exchange fluxes estimated for the time prior to the industrial era, circa 1790. The red number and arrows indicate the perturbation of the carbon during the industrial era. Boxes represent different reservoirs with the number indicating the mass of carbon present in PgC, whilst arrows represent fluxes in PgCyr^{-1} (Ciais et al., 2013).

The effect of human activities on the global carbon cycle was first evident from changing atmospheric CO_2 concentrations at the Mauna-Loa Observatory in Hawaii (Keeling et al., 1976). It is well documented that this increase in atmospheric CO_2 has significant impacts on the global climate. The effect on the carbon cycle took longer to determine (Friedlingstein, 2015). Current Earth system models now include biogeochemical cycles such as the carbon cycle. However, the feedback of a number of processes within these cycles on future climate has yet to be fully assessed (Heinze et al., 2019). The marine biosphere is an important carbon sink. Its future importance is highly uncertain (Friedlingstein, 2015). One of the major uncertainties in the marine carbon sink is the preservation of organic matter in marine sediments. Although only 5% of organic matter exported to marine sediments is ultimately buried, small changes can have large effects on atmospheric CO_2. This process is challenging to monitor and leads to increased uncertainty in climate models. Recent studies have suggested that this process is important and that changing this fraction to 7.5% could account for most of the lower atmospheric CO_2 during glacial periods (Cartapanis et al., 2016).

1.1.1 Marine sediments

Marine sediments, especially along continental margins, are an important store of organic carbon (Hedges et al., 1988, Keil and Hedges, 1993, Hedges and Keil, 1995). The preservation of organic matter in these sediments is important as it allows for the removal of CO_2 and build-up of oxygen in the atmosphere *Figure 1.2* (Mackenzie et al., 2004). As well as providing an essential component of the carbon cycle, preservation of organic matter in sediments also leads to the build-up of fossil fuels and is critical for understanding a number of paleo-environmental markers (Keil and Hedges, 1993).

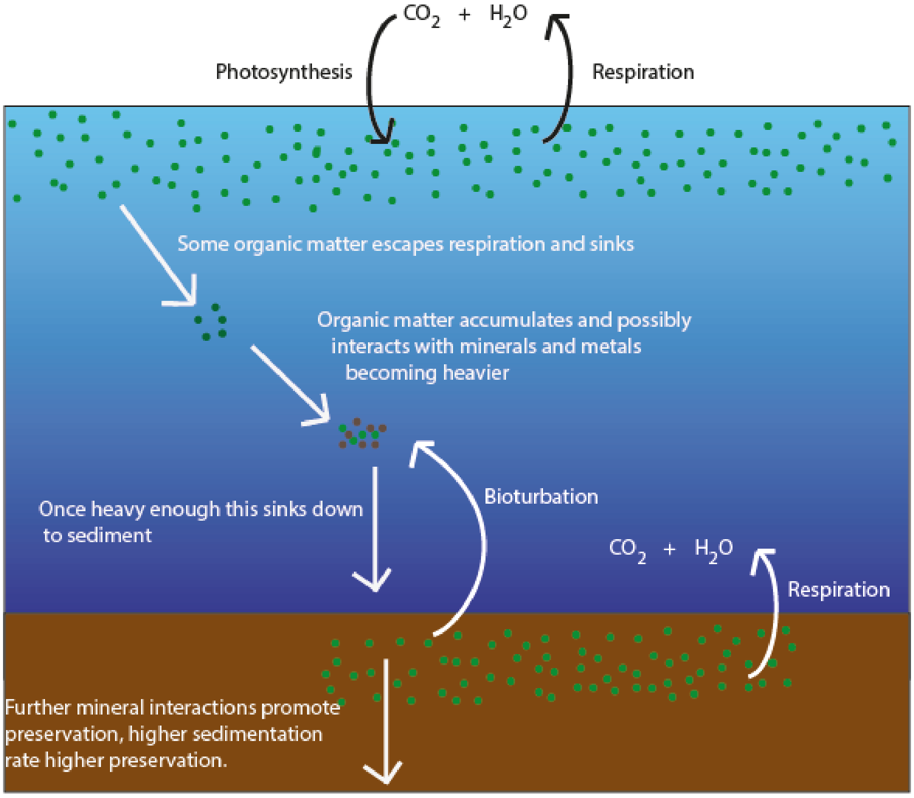


Figure 1.2. Removal of organic matter into marine sediments, removes carbon from the immediate cycling between organic matter and carbon dioxide.

Preservation of organic matter within marine sediments results from a number of different factors. One such factor is the nature of the organic matter, with different compounds thought to have an inherent level of recalcitrance (Hedges et al., 1988). Terrestrial organic matter is especially resistant to degradation meaning that a higher proportion of terrestrial organic matter is preserved than marine. This is because terrestrial organic matter predominately consists of complex structural compounds, such as lignin, which are resistant to degradation, plant pigments and carbohydrates are also resistant to degradation, whereas lipid and sugar are more susceptible to degradation (Hedges et al., 1988). However, the presence of DOM in seawater has been shown to increase the resistance of small molecules to degradation, suggesting that the nature of the organic matter alone is not responsible for whether or not it is preserved (Keil and Kirchman, 1994). In soils environmental factors have been found to have a greater effect on the rate of degradation than organic matter type; factors such as oxygen content, pH and presence of bacteria. This is primarily because these determine the number and type of bacteria present which are able to digest the organic matter and remineralise it into carbon dioxide (Schmidt et al., 2011).These environmental factors are also important in marine sediments with oxygenated sediments showing reduced organic matter preservation and anoxic areas showing increased preservation (Hedges and Keil, 1995). The influence of bacteria is complicated by the production of exopolymeric substances which can promote organic matter preservation (Pacton et al., 2007). Despite the importance of oxygen content on organic matter preservation at a local level, on a global scale the preservation of organic matter seems to be more closely linked to mineral surface area (Hedges and Keil, 1995). It is evident that the factors effecting organic matter preservation in marine sediments are complex and often interlinked, however, evidence suggests that understanding the interactions of organic matter with minerals is vital to understanding the preservation of organic matter in marine sediment (Kennedy and Wagner, 2011, Drouin et al., 2010, Hedges and Keil, 1995).

1.2 Organic matter-mineral interactions

Evidence for the importance of minerals in organic matter preservation comes from a number of observations. First, studies of marine sediments repeatedly observe a strong relationship between mineral surface areas and organic matter content (Keil and Hedges, 1993, Hedges and Keil, 1995, Kennedy et al., 2002, Ransom et al., 1997, Mayer, 1999). Second, a number of laboratory studies have demonstrated that organic matter will bind to minerals and the presence of minerals can reduce organic matter degradation (Curry et al., 2007, Drouin et al., 2010, Saidy et al., 2013, Saidy et al., 2015, Kang and Xing, 2008, Swenson et al., 2015, Aufdenkampe et al., 2001, Lu et al., 2010, Ahmat et al., 2015, Arnarson and Keil, 2000, Shaker et al., 2012, Feng et al., 2005, Mikutta et al., 2007, Ding and Shang, 2010).

Keil and Hedges (1993) determined that more than 80% of organic matter, in sediments along different stages of the Columbia River and estuary, could not be separated from mineral mass by density flotation, whilst Kennedy et al. (2002) noted that 85% of the variation in the amount of organic matter present in black shales could be explained by variations in the amount of mineral surface area. This observed link between mineral surface area and amount of organic matter has been noted in a number of studies and leads to the development of the monolayer hypothesis (Mayer et al., 1985) that posits a single layer of organic matter is bound on the mineral surface. Mayer et al. (1985) analysed sediment samples in an intertidal mudflat, and found a close correlation between the total organic carbon content and mineral surface area throughout the year. This finding was in agreement with previous work, which both used nitrogen adsorption to determine surface area, but still noted the same correlation (Weiler and Mills, 1965, Tanoue and Handa, 1979). These studies suggested this correlation was due to the formation of a monolayer, with a consistent coverage noted at ~1.5 mg of carbon per m^2 of mineral (with some variation caused by the different methods used to measure surface area) (Mayer et al., 1985). However, evidence against this monolayer hypothesis was soon discovered. In 1997 Ransom et al analysed marine sediment samples for total organic carbon (TOC) and determined surface are via N_2 adsorption. Although their samples fit within the ratio expected for monolayer coverage, investigations with transition electron microscopy determined the organic matter present was localised and discontinuous, not in a uniformed monolayer (Ransom et al., 1997). In 1999 Mayer developed a method to determine the degree of coverage using the Brunauer Emmett teller (BET) model, using the fact that the presence of organic matter changes the enthalpy of adsorption. Once calibrated, this method was used to determine the organic coverage of marine sediment samples, determined to be <15%, much less than the 100% that a monolayer would lead to (Mayer, 1999). Even allowing for the considerable potential for error in the calibrations of this method or the misidentification of the organic matter in the transition electron microscopy (TEM) studies, the concept of organic matter as a monolayer was brought into question. Further evidence against the monolayer was provided by Arnarson and Keil (2001), who looked at marine sediments using x-ray photoelectron spectroscopy (XPS) to identify carbon atoms on mineral surfaces. Their results showed carbon atoms are present in discrete spots as opposed to a uniform layer. All these studies and a number of others, however, still noted the consistent ratio between the amount of organic matter and the mineral surface area which they refer to as a monolayer equivalent (Arnarson and Keil, 2001, Mayer, 1999, Ransom et al., 1997, Mayer, 1994b).

1.2.1 Clay minerals

If surface area is not responsible for the amount of organic matter adsorbed, another factor must be limiting the amount of organic matter that can interact. In 1998 Ransom et al investigated the factors affecting the surface area of sediments (Ransom et al., 1998). Here, the theoretical surface area of these sediments, based on the grain sizes, was significantly less than that determined experimentally. It was speculated that this variation was caused by the presence of high surface to volume ratio particles. Using nitrogen adsorption to compare surface area to mineral composition in sediments, a strong correlation was found between surface area and weight percent clay mineral (Ransom et al., 1998). Block and Mayer, determined that the density of different fractions in sediments was consistent with organic matter bound to clay minerals rather than to any heavier minerals (Bock and Mayer, 2000). Arnarson et al expanded on this, using density flotation to separate out samples of different density, with the largest amount of organic matter being present in the lighter fractions. They used x-ray diffraction to identify the minerals and noted a high smectite clay concentration in these organic-rich fractions suggesting that organic matter has a preference for these minerals (Arnarson and Keil, 2001). Further studies have also identified this correlation between organic concentration and clay mineral content (Kennedy and Wagner, 2011, Drouin et al., 2010, Hedges and Keil, 1995, Mayer, 2004) . Drouin et al looked at the interactions that take place between synthetic clay minerals and organic matter, and determined there is a strong interaction between the clays and the organic matter. X-ray diffraction patterns suggested this interaction was adsorption based and not intercalation between the layers, because intercalation would result in a change in the x-ray diffraction pattern which was not observed (Drouin et al., 2010).

1.2.2 Iron minerals

Clay content is not the only factor of importance in organic carbon preservation. Lalonde et al (2012) demonstrated that a large amount of organic carbon present in marine sediments is bound to iron-rich minerals. Samples of sediment from a number of locations were analysed to determine the amount of organic matter bound to iron. The study concluded that approximately 20% of all organic matter in sediments is directly bound to iron (Lalonde et al., 2012). A similar correlation has been noted previously in soils. Kaiser and Guggenberger investigated the amount of organic matter and iron content in topsoils from around Europe. This study revealed a stronger correlation between the amount of iron and the amount of organic matter than between surface area and organic matter (Kaiser and Guggenberger, 2000). A number of more recent studies have also suggested that iron plays a key role in organic matter preservation in soils (Zhang et al., 2013, Wang et al., 2013). This importance in soils together with Lalonde's work suggests that iron may play an important role in organic matter preservation in marine sediments.

A number of laboratory-based studies into the interactions between iron, particularly iron hydroxides, and organic matter have been undertaken. In 2014 Barber et al. incubated organic matter and iron together under different redox conditions, and monitored the stable carbon isotope signature of the solid phase to monitor the uptake of the fresh organic matter (Barber et al., 2014). The presence of the iron significantly increased the rate the organic matter moved from the dissolved to solid phase. This effect was particularly pronounced when the iron was present under oxidising conditions which favour the formation of iron hydroxides. The samples with iron present, particularly as iron hydroxide, showed the least degradation after 250 days (Barber et al., 2014). This result is consistent with the earlier work during which it was found that, using ^{14}C-labelled organic matter, organo-iron complexes degraded much more slowly than free organics (Boudot et al., 1989). Swenson et al. developed further on this work, although looking at organic matter in the context of soils, to investigate which types of organic matter bound best to synthetic ferrihydrite. The ferrihydrite was incubated with organic matter extracted from bacteria and liquid chromatography and mass spectrometry used to monitor and identify the organic matter remaining in solution. Organic matter with the highest affinity for ferrihydrite were those with phosphate groups, followed by those with di-carboxylate groups and those with aromatic or nitrogen-containing groups (Swenson et al., 2015). The fact that organic matter with specific functional groups interacts more readily with the iron hydroxides suggests that interactions involve some stronger chemical interaction such as direct chelation or coordination (Lalonde et al., 2012).

Studies in soils have suggested that clays and iron minerals may be interacting together causing stronger interactions with organic matter. Wiseman and Puttmann (2006) investigated 5 soil samples from Germany, using x-ray diffraction to identify mineral composition, elemental analysis to determine the amount of organic matter present and dithionate extraction to determine the iron content. Using statistical analysis they determined correlation between these three parameters and although the results varied between the different soils, there was generally a strong correlation observed between all three. The authors speculate this correlation shows the organic matter is binding to the iron hydroxides which are binding to the clay minerals, with the positively charged iron hydroxides bringing together the clays and organic matter which would both be negatively charged under the conditions employed. However they acknowledge that a statistical relationship is not sufficient to fully support this hypothesis, considering all three variables have previously been shown to correlate with other factors such as surface area (Wiseman and Puttmann, 2006, Dumig et al., 2012). Work carried out by Saidy et al. (2015) adds further evidence to this hypothesis of interaction among clay minerals, iron hydroxides and organic matter. These authors used gas analysis to monitor the degradation of organic matter bound to different clay minerals, with and without iron hydroxides present. Addition of the iron hydroxides lead to a change in the surface area and the cation exchange capacity of the minerals, although the degree of change depended on the type of iron hydroxide with ferrihydrite having the largest effect. Sorption of the organic matter to all the clay minerals results in the observed reduction in degradation compared to unbound organic matter. The clay mineral with a ferrihydrite coating showed an even greater reduction in degradation than the uncoated mineral (Saidy et al., 2015). However, given that a mixture of organic matter was used, it may be some of the organic matter is binding to the clay and some to the iron hydroxide leading to the observed increase in amount of organic matter preserved. Further work would need to be carried out to see if this is the case or not; this could be done by monitoring which organic compounds are adsorbing to the clay minerals, and whether the presence of the iron hydroxide changes this or not. This could also be investigated by looking at which functional groups bind best to clays and iron hydroxides separately. All of these studies were carried out under soil conditions so it would be instructive to repeat them under conditions found in marine sediments.

1.2.3 Organic matter

Functional group specific interactions suggest the nature of the organic matter is also important in determining the interactions that take place with minerals. Komada and Reimers (2001) hypothesised that only a proportion of organic matter binds strongly to minerals with the remainder loosely bound and able to desorb. Satterberg et al. (2003) also hypothesised that the organic matter present affects what proportion initially sorbes to the mineral. A variety of functional groups have been found to be preferentially sorbed to minerals. Kang and Xing (2008) investigated humic acid binding to goethite and found that more polar compounds were preferentially bound. Swenson et al. (2015) looked at microbial metabolite and ferrihydrite and found strongest interactions with phosphate-containing compounds followed by those with carbonyl groups and those containing nitrogen and aromatic functionalities. Similar results were found by Newcomb et al. (2017) in mica, finding carbonyls and phosphate group were favoured followed by nitrogen-containing groups. In goethite the nitrogen groups were found to be most favoured, in both minerals alkanes were the least favoured. Aufdenkampe et al. (2001) also found a preference for nitrogen-rich compounds when looking at the interactions of organic matter and riverine sediments and kaolinite. Lu et al. (2010) looked at kaolinite and montmorillonite with algal lipid extracts and found that fatty acids bound more strongly than n-alkanes, Ahmat et al. (2015) also found a preference for fatty acids when investigating the sorption of organic matter from the water column to montmorillonite and kaolinite.

Different studies have identified various functional groups as important in organic matter-mineral interactions, however, it is important to consider the differences between these studies. For example, studies using spectroscopic techniques to identify functional groups are limited by the analytical window of the instrument used. Studies using chemical standards often do not account for all functional groups. Furthermore, different minerals and different conditions are likely to favour different functional groups. However, the overall trend suggests more polar compounds interact more strongly than non-polar compounds.

1.2.4 Mechanism

The nature of the interactions between the organic matter and the mineral is also important to consider, this is likely to vary for different minerals and different types of organic matter. The mechanism of organic matter-mineral interactions determines how strongly organic matter is bound, and therefore the length of time over which it is likely preserved (Henrichs, 1995). Understanding mechanistic details of these interactions is therefore vital for determining the role that mineral interactions play in organic matter preservation. Many studies have investigated this mechanism using the fact that different mechanisms are promoted under different conditions. A study by Arnarson and Keil (2000) for instance used different background solutions to promote and inhibit different mechanisms, Na_2SO_4 to inhibit ligand exchange, $CaCl_2$ to promote cation bridging and NaCl to provide a background. Further insight was provided by investigating the enthalpy of bound matter, by changing the temperature and changing the hydrophobicity of acid compounds by changing the pH. This approach determined that the majority of the bonding was due to Van der Waals interactions, ligand exchange and cation bridging (Arnarson and Keil, 2000). Feng et al. (2005) used a similar method to investigate the interactions of humic acids with montmorillonite and kaolinite, estimating ligand exchange accounted for 32% of bonding, van der Waals 22% and cation bridges 41% when Ca^{2+} was the background electrolyte. Mikutta et al. (2007) carried out a similar study using soil organic matter and three different minerals. Goethite was found to bind predominately via ligand exchange with little contribution from Van der Waal forces and no detectable contribution from cation bridging or Ca-OM precipitation. Pyrophyllite was found to have a smaller portion attributed to ligand exchange and around half attributed to Van der Waal forces. Vermiculite was found to bind with predominately cation-bridging with very little contribution from ligand exchange. Aromatic fractions seem to generally be more favourably adsorbed when cation-bridging is dominant (Mikutta et al., 2007). All of these studies suggest that ligand exchange, cation bridging, and Van der Waals interaction are important in organic matter-mineral interactions, however the nature of the organic matter and mineral affects which are of greatest importance.

1.3 Aim of this study

The primary aim of this thesis is to address the question of how different organic matter functional groups interact with the mineral kaolinite, under different organic matter-mineral ratios. As well as investigating the effect of molecular weight within one functional group. The organic matter used by previous studies has largely been dissolved, but particulate organic matter can also be a major source of organic matter to sediments (Lee et al., 2009). The use of only dissolved organic compounds has limited the range of functional groups available. However, the inclusion of insoluble organic matter presents significant methodological difficulties, specifically in separating bound and non-bound organic matter. It will therefore be necessary to develop a method capable of achieving this. The development and testing of this method together with the methods used throughout this thesis is discussed in Chapter 2. Chapter 3 will then aim to address aim one by investigating the role of organic matter type on organic matter-mineral interactions. This will be achieved by investigating the sorption of organic matter with different functional groups and molecular weights to the clay mineral kaolinite.

The second aim of this thesis is to investigate how different functional groups are influenced by changing binding conditions. These changes can then be used to infer which mechanisms are responsible for the sorption of different components of the organic matter. Previous studies have focussed on either the composition of organic matter bound to minerals, or the mechanism by which it is bound. These two factors are intricately linked because it is the functional groups present on the organic matter and the nature of the mineral that determines the mechanism. Chapter 4 will investigate the mechanism by which the different functional groups interact with kaolinite

The third aim is to expand these studies to other clay minerals and iron hydroxides. Both clay and iron minerals have both been shown to be important in organic matter-mineral interactions in marine sediments (Lalonde et al., 2012, Mayer, 2004). However, the preference for one type of organic matter over another can also vary between mineral types, as can the mechanism of interaction (Newcomb et al., 2017, Mikutta et al., 2007). It is therefore important to consider the nature of the organic matter when looking at the effect of different minerals on organic matter sorption. This will be achieved in Chapter 5 which will investigate the interactions of different molecules with bentonite and goethite and compare these with the result with kaolinite from earlier chapters.

The fourth aim is to investigate how widely applicable these results are, within both marine and terrestrial environments. This will be done, in Chapter 6, by investigation the sorption of organic matter extracted from three different sources with kaolinite, bentonite and a natural soil assemblage.

Finally, Chapter 7 will serve as a summary of previous chapters as well as allowing the discussion of further work in the study of organic matter-mineral interactions in marine sediments.

Chapter 2 Materials and Methods

The aim of this study is to further the understanding of organic matter-mineral interactions within marine sediments. In particular, the goal is to investigate the mechanisms at work and the effects of organic matter (both particulate and dissolved) and mineral type. In order to do this, it is necessary to develop a method capable of separating bound and unbound organic matter that could be used under a variety of conditions with an array of minerals and organic matter sources. This chapter outlines the basic method and how it was adapted for different chapters. It also summarises how the method was validated to ensure that results obtained are indeed reflective of bound organic matter, as well as how all starting materials are characterised.

2.1 Initial work

2.1.1 Organic matter and mineral sources

Phytoplankton are a significant contribution to marine organic matter, and the bulk composition of organic matter reaching the deep ocean differs little from that of surface phytoplankton (Hedges et al., 2001). Consequently, preliminary experiments were carried out using phytoplankton as the organic matter source. *Tetraselmis suecica*, a marine green algae, was chosen as it is widespread throughout the oceans around Europe and Asia, and lacks any silica or carbonate components which could impact its interactions with sedimentary minerals (Guiry, 1996, Le Moigne et al., 2013).

Phytoplankton were grown at 20 °C on a 12h:12h light:dark cycle, bubbled continuously with 0.2 micron filtered air. The culture medium used was Walne's, a nutrient and vitamin solution, which was xenic, meaning multiple species could be present. Phytoplankton were harvested during the exponential growth stage by centrifugation followed by freeze drying.

Clay minerals and iron oxides have been suggested as the main minerals of importance for organic matter preservation (Saidy et al., 2015). Initially this project focused on clays because these are more common within the marine environment, with kaolinite being one of the most ubiquitous (Porrenga, 1967). Kaolinite was obtained from Fischer Scientific as pure kaolin with a grain size of 1-1.8 µm. Prior to sorption experiments kaolinite was heated to 400°C to remove any native organic matter.

2.1.2 Instrumentation

Analysis of organic matter was primarily carried out by gas chromatography-mass spectrometry (GC-MS) and a standard procedure was developed. Column chromatography to separate the polar, nonpolar and aromatic fractions was not performed, because it was determined that this provided limited separation of the organic matter. GC-MS of the total lipid extract produced baseline peak separation.

Gas chromatography was performed on a Trace 1310 Gas Chromatograph coupled to a TSQ 8000 triple quadrupole mass spectra (Thermo Scientific). The GC was fitted with a DB 5 column, 30 m in length, with a 0.250 mm diameter and a 0.10 µm film. The column was held at 40 °C for 2 minutes then increased to 310 °C at a rate of 6 °C min^{-1}, before being held at 310 °C for a further 15 minutes. 1 µL of sample was injected in split mode, split ratio 6.7 at 50 °C, the carrier gas was helium at 2 mL min^{-1}. Electron ionisation at 70eV was used in the mass spec scanning from M/Z 50-650. Solid extraction prior to GC-MS was carried out at 100 °C with 9:1 DCM: methanol on an automated solvent extractor, and quid-liquid extraction in a separating funnel with 3×30 mL DCM.

Tetraselmis samples were derivatised with N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA). Derivatisation was necessary because the samples contained polar compounds. Derivatisation with BSTFA converts OH groups into silyl groups (*Figure 2.1*). To ensure sufficient derivatisation, sensitivity experiments were conducted to determine the optimal amount of derivatisation required to achieve maximum peak height of the 2-methyloctadecanoic acid. GC results were interpreted by using internal and external standard to convert peak areas to concentrations.

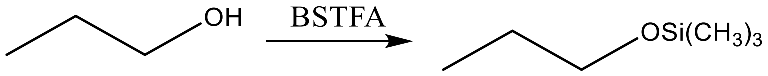


Figure 2.1. Derivatisation reaction used on Tetraselmis *extracts to convert OH groups into silyl groups increasing response factor of polar compounds in GC-MS analysis.*

Elemental analysis was performed on an Elementar Vario Isotope Cube Elemental Analyser in CN mode equipped with a Thermal conductivity detector, with samples combusted at 950 °C. The mineralogy of the solid phases was determined by X-ray diffraction (XRD) using a Panalytical X'Pert pro diffractometer machine fitted with a Cu X-ray tube, operating at 35 kV, 40 mA utilising automatic slits and a step size of 0.02º 2θ at 1 second/ step. Semi-quantitative analysis was undertaken using a least squares method similar to that used in the Microsoft Excel-based programs RockJock (Eberl, 2003), and FULLPAT (Chipera and Bish, 2002). Surface areas were determined with nitrogen absorbance using the Brunauer-Emmett-Teller (BET) method on a micromeritics 3 flex 3.02 at 77 K.

2.1.3 Analysis of starting materials

The *Tetraselmis suecica* extract was analysed using elemental analysis and GC-MS. The elemental analysis results show a composition of 7.9% nitrogen and 46.1 % carbon whereas the primary components of the *Tetraselmis suecica* extract in the GC-MS results are fatty acids and terpenoids *Figure 2.2*. This is consistent with previous studies of marine microalgae (Soto-Leon et al., 2014, Abomohra et al., 2017). Absence of organic nitrogen-containing compounds suggests that any nitrogen-containing molecules are not sufficiently volatile to be detected by GC-MS. The presence of ammonium ions detected by ion chromatography also suggest that some of the measured elemental nitrogen is present as inorganic nitrogen.

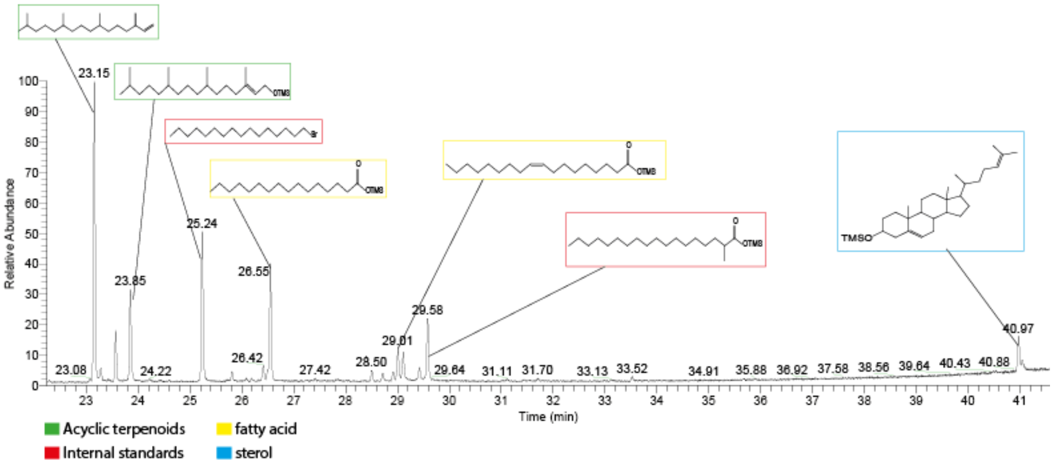


Figure 2.2. Chromatogram of total lipid extract of Tetraselmis suecica *highlighting major compounds and compound groups.*

Kaolinite was analysed by XRD to determine composition and BET to determine surface area. The X-ray diffraction (XRD) composition of kaolinite was 72.9% kaolinite, 23.8% illite and 6.3% quartz. The BET surface area of kaolinite was 16.3m^2g^{-1}.

2.1.4 Experimental set up

During sorption experiments the mineral and organic matter were combined in glass reaction vessels which were heated to 400 °C overnight to remove any organic matter present (*Figure 2.3* and *Figure 2.4*). A flow of hydrated nitrogen was used to keep the organic matter and mineral in suspension. (In future experiments other gases could be employed to investigate the effects of oxic and anoxic conditions.) Previous studies, based on dissolved organic matter (DOM; i.e., organic matter capable of passing through a glass fibre filter (GF/F) with a pore size of 0.7 µm), collected the bound material by centrifugation (Wang and Lee, 1993, Ding and Henrichs, 2002, Schneckenburger et al., 2018, Avneri-Katz et al., 2017, Mikutta et al., 2007, Feng et al., 2005, Swenson et al., 2015, Liu and Lee, 2006, Meier et al., 1999, Yeasmin et al., 2014, Shaker et al., 2012, Arnarson and Keil, 2000, Tipping, 1981, Saidy et al., 2013) or filtration (Schneckenburger et al., 2018, Mikutta et al., 2007, Meyers and Quinn, 1973, Ding and Shang, 2010, Saidy et al., 2013). The presence of particulate organic matter (POM; i.e., organic matter not capable of passing through a glass fibre filter (GF/F) with 0.7 µm pore size) in this study made this option unviable. Therefore, density fractionation was used to separate the mineral-bound organic matter and the non-bound particulate organic matter from these reaction vessels. A kaolinite suspension of 50 gL^{-1} in milliQ water and a *Tetraselmis suecica* suspension of 0.2 mgmL^{-1} in milliQ water were prepared. For the clay samples these two suspensions were combined in equal proportions; for the *Tetraselmis suecica* blanks the clay suspension was replaced with milliQ water ensuring concentrations remained constant. A relatively high organic matter concentration was used so that organic matter was in excess of the mineral binding sites, resulting in competition between the different molecules for these sites. Preliminary experiments were conducted to assess the suitability of the separation method, binding did not need to occur, therefore the suspensions were left for only 5 minutes rather than the 2 hours previously shown to be required for sorption (Arnarson and Keil, 2000). Density fractionation was carried out using sodium iodide at 1.6 gmL^{-1}, on the pellet resulting from the initial centrifugation (*Figure 2.5*). This was carried out using a clay sample and a *Tetraselmis suecica* blank with density fractionation free repeats on both samples.

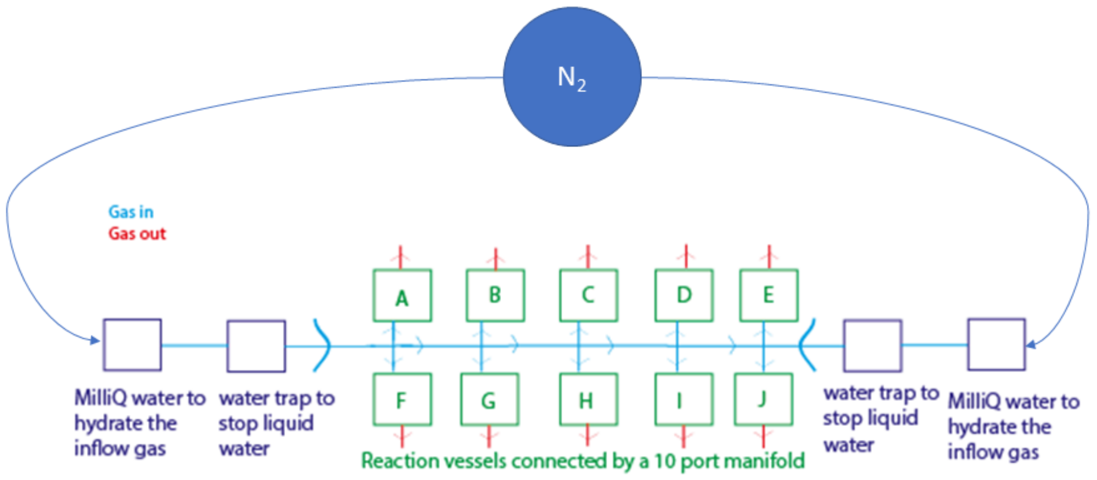


Figure 2.3. Reaction vessel set-up used for sorption experiments. Nitrogen was provided by a nitrogen generator, before being bubbled though a hydration vessel and a water trap. Hydration of nitrogen was necessary to reduce evaporation within reaction vessels, whilst the water trap prevented liquid water blocking the nitrogen input into the 10 reaction vessels.

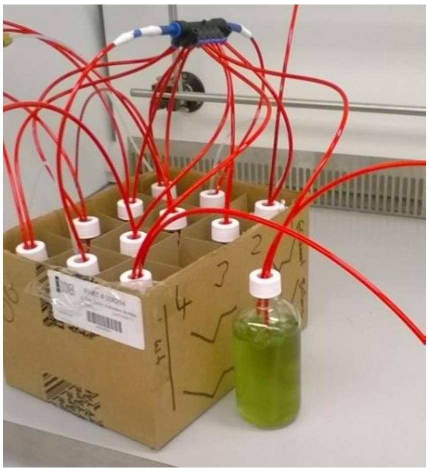


Figure 2.4 Photograph of the reaction set up illustrated in Figure 2.3.

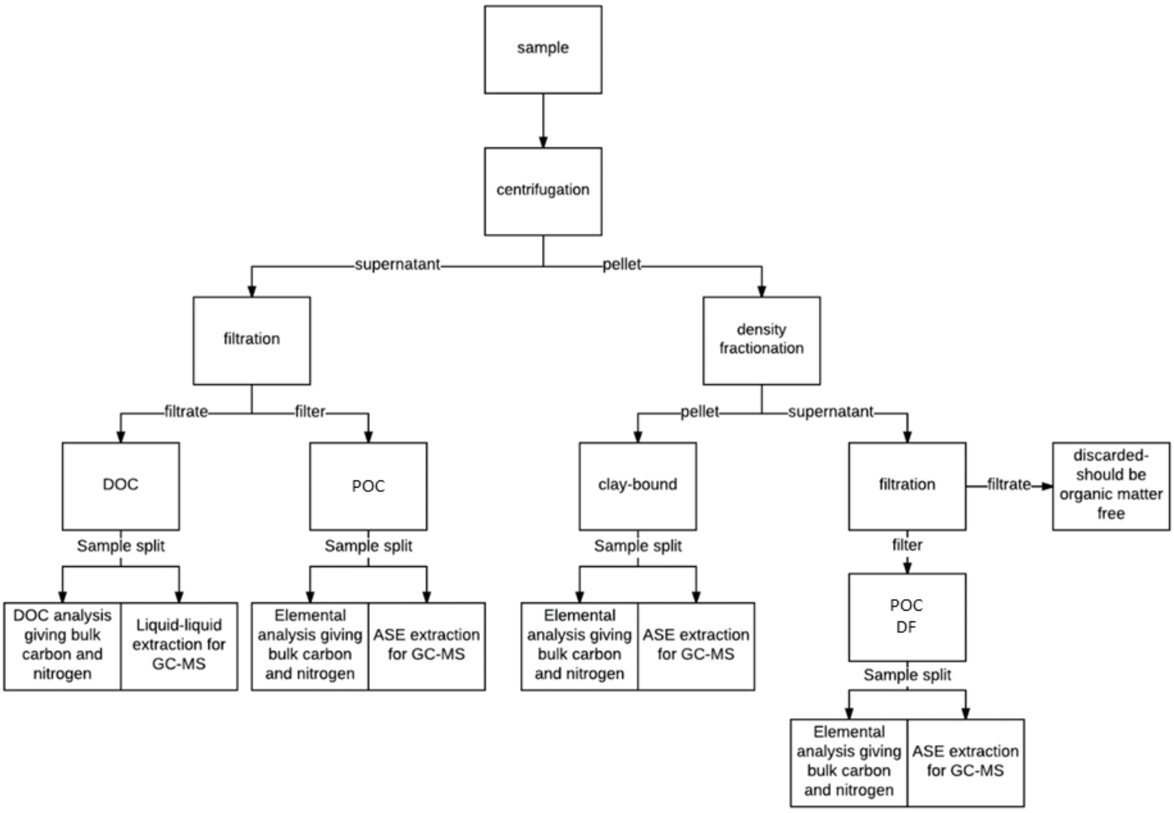


Figure 2.5. Flow diagram of the process in the density fractionation experiment.

The density fractionation successfully removed the particulate organic matter from the centrifugation pellet in the absence of clay, suggesting this fraction should represent the clay-bound matter. The carbon and nitrogen content of this fraction can be seen in *Figure 2.6* and *Figure 2.7*. The clay appears to bind some organic matter, in spite of the short reaction time, with an increase in both carbon and nitrogen content within this fraction in presence of clay. A slight preference for nitrogen-containing organic matter was noted, with nitrogen percentage in the clay fraction higher than carbon, consistent with previous findings (Aufdenkampe et al., 2001).

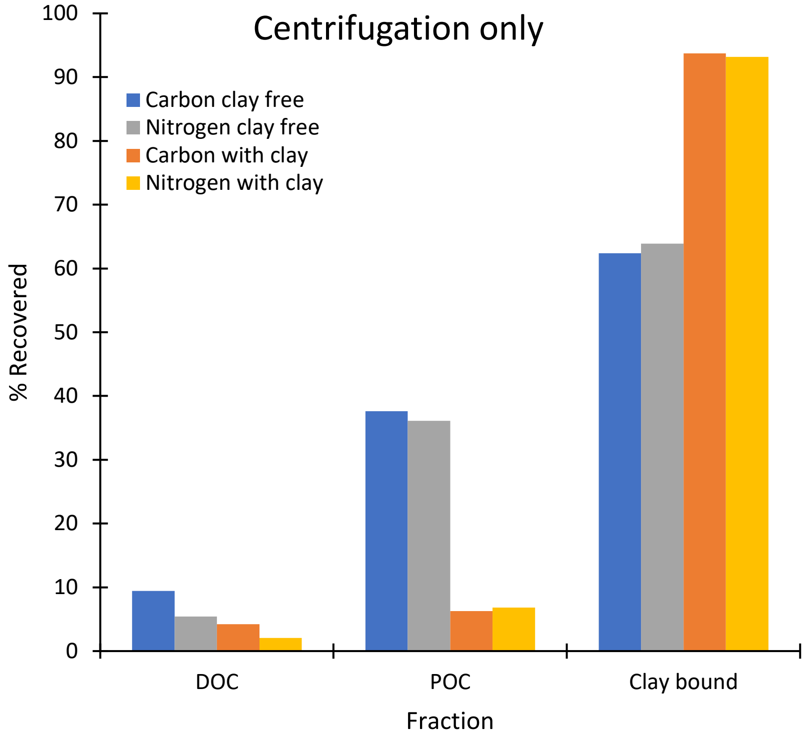


Figure 2.6. Elemental analysis of the centrifuged pellet. A notable amount of both carbon and nitrogen can be seen in the "clay bound" fraction even in absence of clay suggesting centrifugation alone is insufficient to separate bound and unbound organic matter.

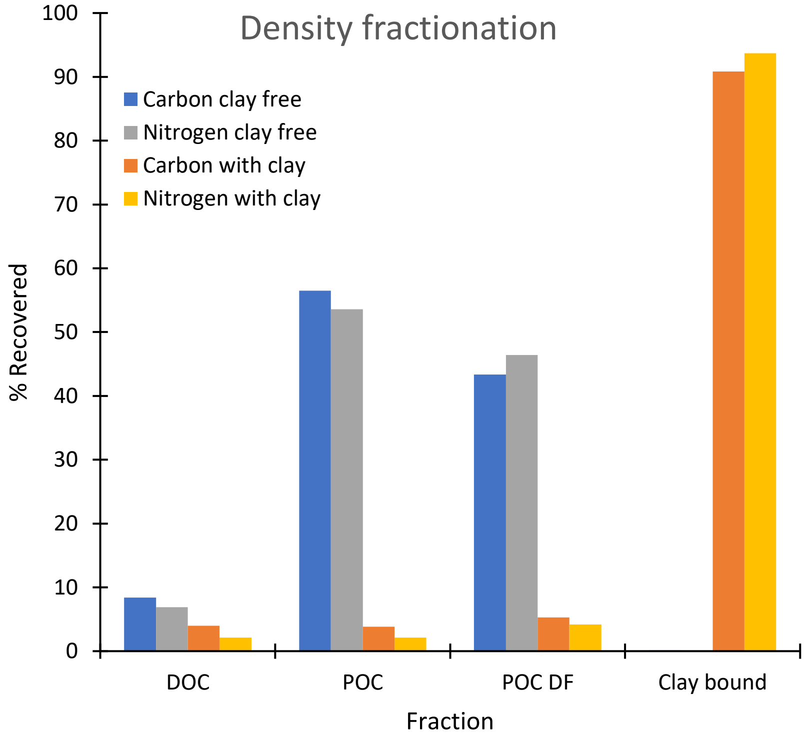


Figure 2.7. Elemental analysis of the density fractionated pellet. The "clay bound" fraction in absence of clay, appears to show no carbon or nitrogen suggesting density fractionation is sufficient to separate bound and unbound organic matter.

Experiments were also carried out to determine the extent of degradation over the course of the sorption experiment. Mineral-free reaction vessels were prepared and left bubbling under nitrogen for 0, 25 and 192 minutes, after this time the dissolved and particulate organic carbon were measured. Results shown in *Figure 2.8* demonstrate that even after 192 hours minimal degradation is occurring under the conditions of the experiment.

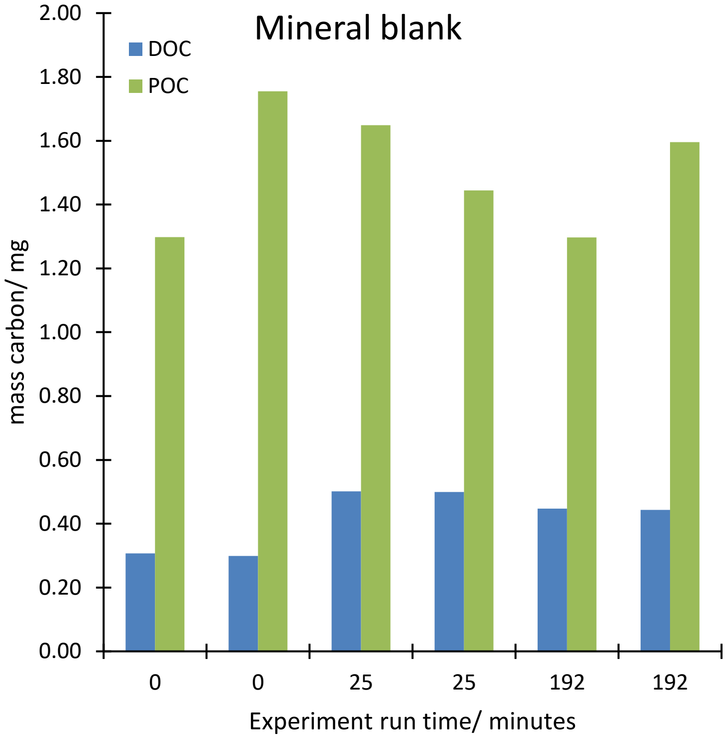


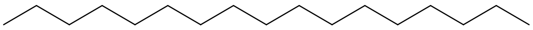
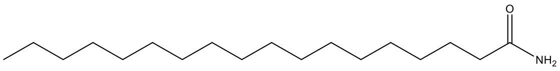
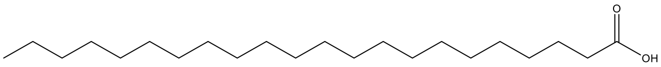
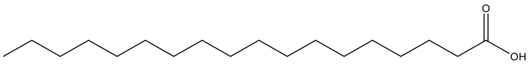
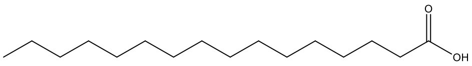
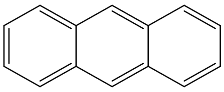
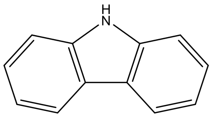
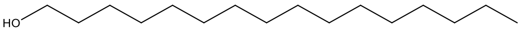
Figure 2.8. Assessing the amount of degradation. Dissolved and particulate carbon masses after different reaction times in the absence of mineral.

2.2 Standards work

2.2.1 Organic matter and mineral sources

In order to reduce the complexity of the system, allowing more focus on the effect of the functional groups and to increase the range of functional groups available, later work focused on specific compounds. Previous studies have shown that both organic matter type and molecular weight can impact on the amount of organic matter/mineral binding, and this study attempts to disentangle these two effects (Kang and Xing, 2008, Swenson et al., 2015, Aufdenkampe et al., 2001, Lu et al., 2010, Ahmat et al., 2015, Arnarson and Keil, 2000). Compounds were chosen to represent major functional groups: alcohol, aromatic, amide, fatty acid and alkane and to have a similar number of carbon atoms. Further experiments were carried out to investigate the effect of molecular weight used, compounds with identical functional group, and varying carbon count. All compounds were obtained from Sigma Aldrich. Details of each compound can be found in *Table 2.1*.

Table 2.1 Compounds used as example organic matter in experiments.

Compound	Functional group	Number of carbons	Structure
Heptadecane	Alkane	17	
Octadecanamide	Amide	18	
Behenic acid	Fatty acid	22	
Stearic acid	Fatty acid	18	
Palmitic acid	Fatty acid	16	
Anthracene	Aromatic	14	
Carbazole	Aromatic	12	
Hexadecanol	Alcohol	16	

In these experiments a variety of clay and iron minerals were used, with kaolinite being the primary mineral, and bentonite, goethite and ferrihydrite used when investigating the impact of different mineral sources on organic matter binding. As discussed in section2.1.1, kaolinite was used as the main mineral because of its abundance in marine sediments. Clays are formed of two different types of aluminosilicate sheets, tetrahedral and octahedral. These sheets can be arranged in 2 ways, 1:1 tetrahedral: octahedral, or 2:1 tetrahedral: octahedral: tetrahedral. In 1:1 clays the sheets are generally uncharged where as in 2:1 clays the sheets have a net negative charge, these differences have the potential to influence the binding interactions to the different types of clay (Newman, 1987). For this reason, will be compared in Chapter 5. Bentonite was chosen to represent a 2:1 clay mineral, in comparison with kaolinite which is 1:1. Goethite and ferrihydrite represent iron oxide minerals which as well as clays have also been shown to interact strongly with organic matter. Goethite is representative of a highly crystalline iron oxide whilst ferrihydrite is amorphous (Cornell and Schwertmann, 2003). These differences in crystallinity are likely to impact on the number and nature of potential binding sites. Kaolinite was obtained from Fischer Scientific as pure kaolin, with a grain size of 1-1.8 µm. Bentonite was obtained from the British Drug Houses Ltd, BDH laboratory Chemicals Division, Poole. Goethite was obtained from Sigma Aldrich, and ferrihydrite was synthesised using the method of (Cornell and Schwertmann, 2003). To remove any native organic matter the two clays were heated to 400°C over-night, however as this treatment would result in structural changes to the iron oxides these were instead treated with hydrogen peroxide.

2.2.2 Instrumentation

Analysis of organic matter was carried out by gas chromatography-mass spectrometry (GC-MS). Column chromatography to separate the polar, nonpolar and aromatic fractions was not performed because mixtures were not sufficiently complex to warrant it.

Gas chromatography was performed on a Trace 1310 Gas Chromatograph coupled to a TSQ 8000 triple quadrupole mass spectra (Thermo Scientific). The GC was fitted with a DB 5 column, 30 m in length, with a 0.250 mm diameter and a 0.10 µm film. The column was held at 40 °C for 2 minutes then increased to 310 °C at a rate of 6 °C min^{-1}, before being held at 310 °C for a further 15 minutes. 1 µL of sample was injected in split mode, split ratio 6.7 at 50 °C, the carrier gas was helium at 2 mL min^{-1}. Electron ionisation at 70eV was used in the mass spec scanning from M/Z 50-650. Extraction prior to GC-MS was carried out at 100 °C with DCM on an automated solvent extractor. It was determined that derivatisation was not necessary, as all standards gave a linear response without derivatisation. GC results were interpreted by using external standards to convert peak areas to concentrations.

The mineralogy of the solid phases was determined by X-ray diffraction (XRD) using a Panalytical X'Pert pro diffractometer machine fitted with a Cu X-ray tube, operating at 35 kV, 40 mA utilising automatic slits and a step size of 0.02º 2θ at 1 second/ step. Semi-quantitative analysis was undertaken using a least squares method similar to that used in the Microsoft Excel-based programs RockJock (Eberl, 2003), and FULLPAT (Chipera and Bish, 2002). Surface areas were determined with nitrogen absorbance using the Brunauer-Emmett-Teller (BET) method on a micromeritics 3 flex 3.02 at 77 K.

2.2.3 Analysis of starting materials

Standards which were going to be used in combined experiments were analysed to ensure that baseline separation could be achieved (*Figure 2.9*) and that a linear response was obtained with increasing concentration (*Figure 2.10*). This result was achieved for the six main standards. The remaining compounds were used only in isolation hence base line separation was not required, however all show a linear concentration response (*Figure 2.11*).

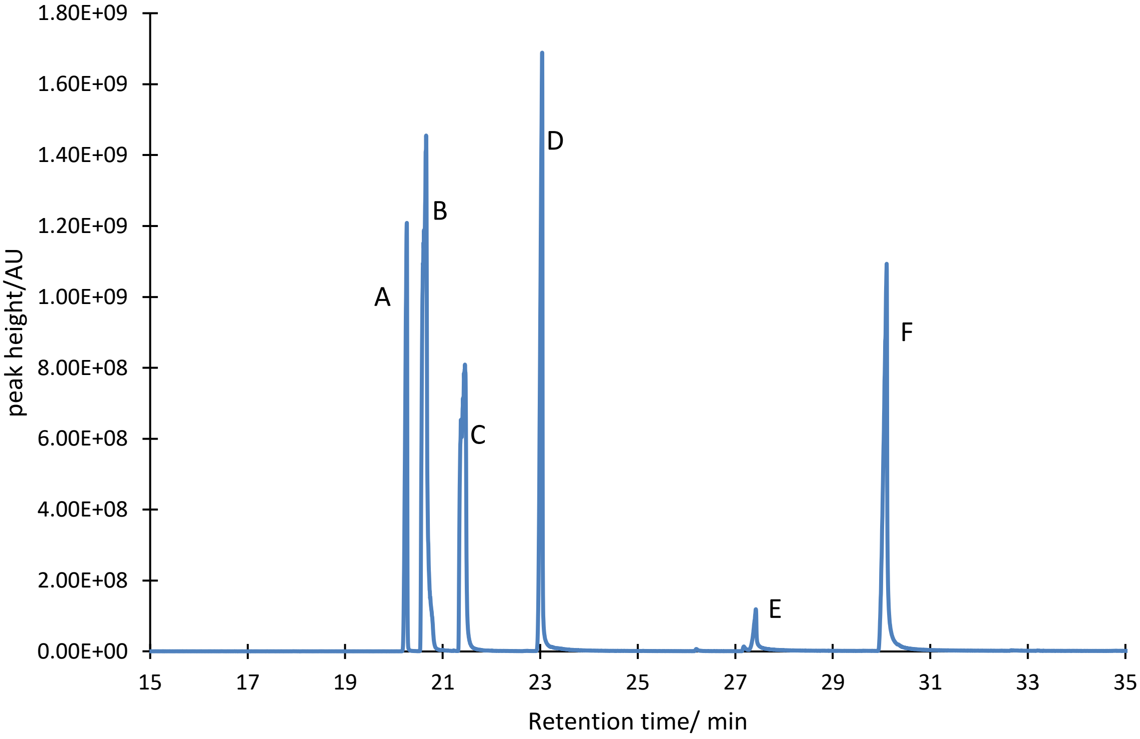


Figure 2.9. GC trace for the six main standards used in Chapter 4 and 5 demonstrating the baseline separation. Peaks A: Heptadecane, B: Anthracene, C: Carbazole, D: Hexadecanol, E: Stearic Acid, F: Octadecanamide.

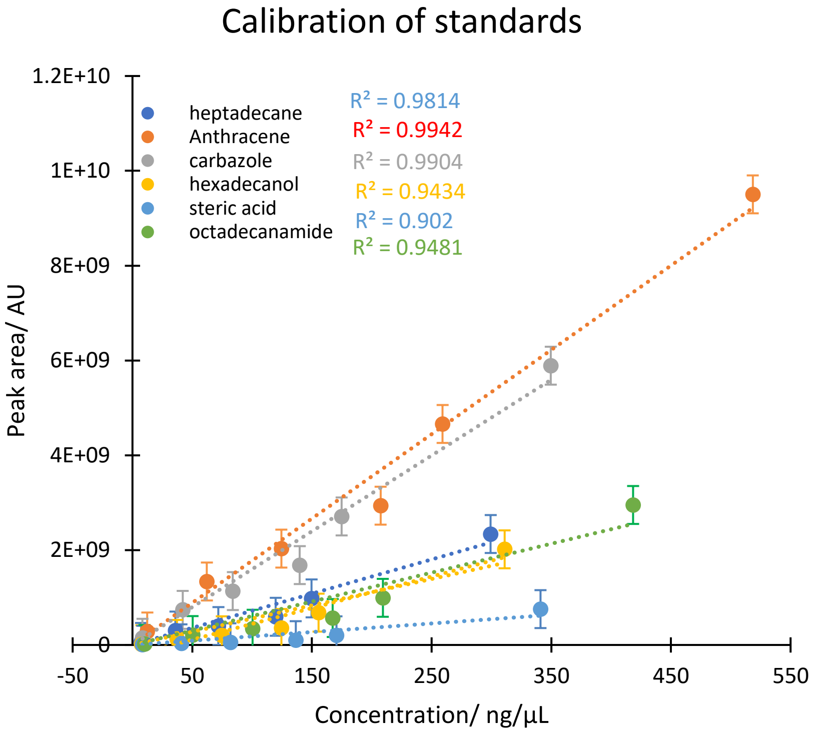


Figure 2.10. Calibration of the six main compounds used in chapters 3, 4 and 5. Illustrating a linear relationship between concentration and peak area.

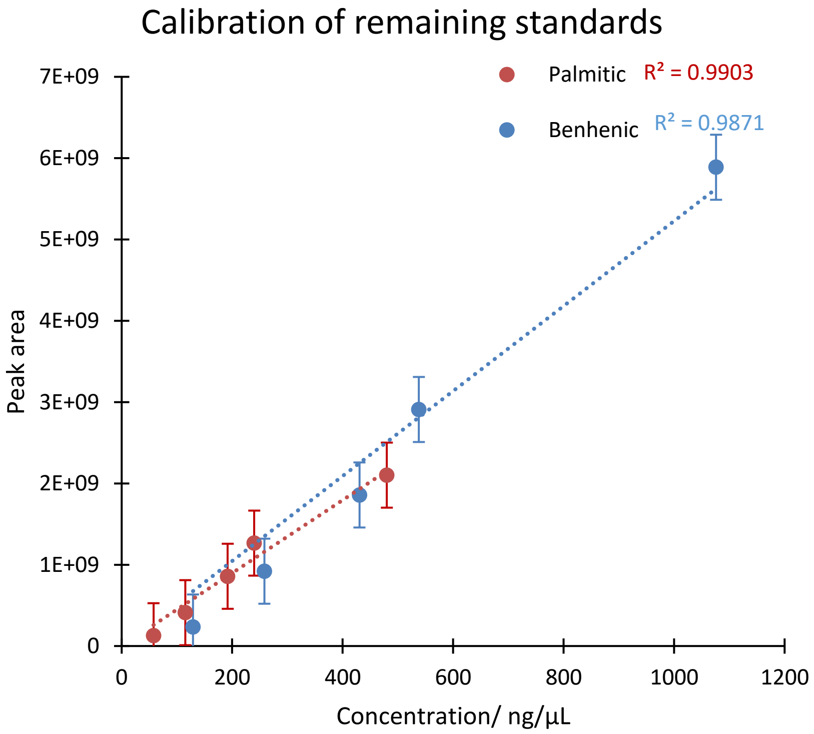


Figure 2.11. Calibration of remaining compounds used in chapter 3. Illustrating a linear relationship between concentration and peak area.

All minerals were analysed by XRD to determine composition and BET to determine surface area. The X-ray diffraction (XRD) composition of kaolinite was 72.9% kaolinite, 23.8% illite and 6.3% quartz. For bentonite the XRD composition was 89.1% montmorillonite (swelling clay), 9% albite, 1.9% quartz. In the goethite sample, goethite was the only detectable mineral. In the ferrihydrite sample there were no detectable peaks, but a high background which is consistent with an amorphous iron-rich compound. The results of BET surface area measurements can be seen in *Table 2.2*

Table 2.2. Surface area and composition of minerals used in standards experiments.

Mineral	BET Surface area/ m²/g	XRD composition
Kaolinite	16.3	72.9% kaolinite, 23.8% illite and 6.3% quartz
Bentonite	12.4	89.1% montmorillonite, 9% albite, 1.9% quartz
Ferrihydrite	259.2	Peaks consistent with amorphous iron-rich compound
Goethite	15.3	Goethite only detectable mineral

2.2.4 Experimental set up

Standard experiments were carried out in reaction vessels under hydrated nitrogen as in section 2.1.4, however the low masses of organic matter required for the experiments necessitated the preparation of stock solutions for dispensing the required amounts. As the compounds were not water soluble, these stock solutions were made up in isopropyl alcohol (IPA). Once the organic matter had been added, the reaction vessels were left bubbling with nitrogen causing the volatile IPA to evaporate and leaving the standard suspended in the water, at which point the clay was added.

Although the density fractionation successfully separated the bound and unbound organic matter the high ionic strength of the sodium iodide solution had the potential to influence the binding, especially in the experiments explicitly looking at how different solution conditions affect the binding. For this reason and because the standards appeared to be less dense, experiments were carried out to see if centrifugation alone was sufficient to separate the bound and unbound standards, as illustrated in *Figure 2.12*. This was carried out with various standards and all showed very low concentration in the centrifugation pellet in the absence of clay. The results for heptadecane are shown in *Figure 2.13*.

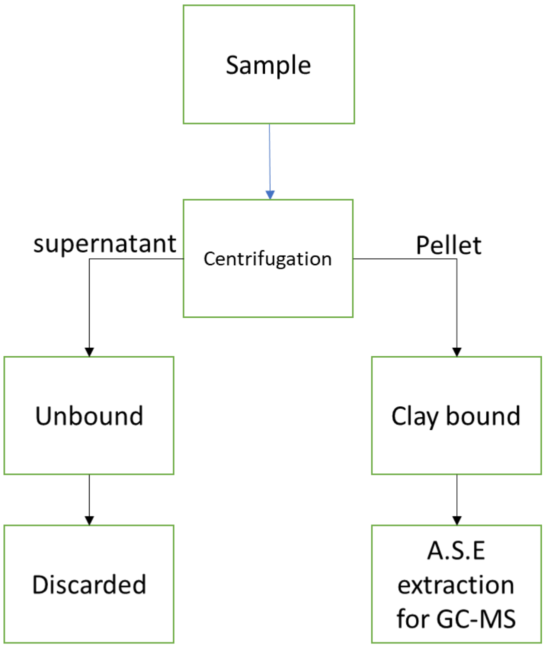


Figure 2.12. Flow diagram of the separation process in the standard experiments.

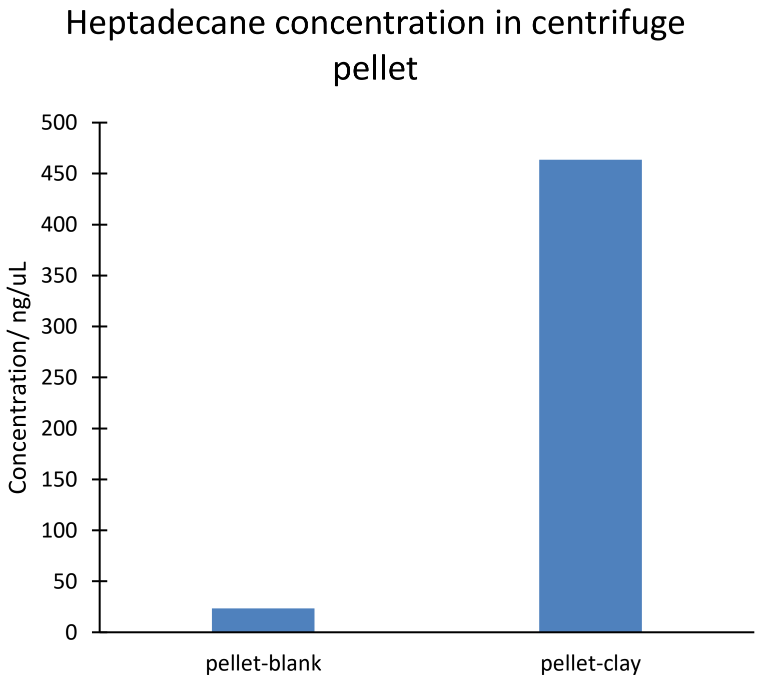


Figure 2.13. Concentration of heptadecane in centrifugation pellet inclusive and non-inclusive of clay.

It was also determined that the 9:1 DCM: methanol mixture used for extraction in the initial experiments resulted in salt being present in the extracts. In order to alleviate this problem, the standards were extracted with DCM only. The extraction efficiency of this DCM only method was tested and found to be 84%. Where error bars are presented these were calculated for individual compounds using the standard deviation of repeats.

2.3 CEH Work

2.3.1 Organic matter and mineral sources

Work undertaken at the Centre of Ecology and Hydrology in Bangor concentrated on studying the effect of different organic matter: mineral ratios on binding between different natural mineral and organic matter sources. This work focused on the dissolved fraction of the organic matter, i.e., able to pass through a GF/C filter with a nominal pore size of 0.45 µm. There are a number of classification methods for dissolved organic matter (DOM), such as molecular weight (Arnarson and Keil, 2000), photic properties (Ding and Shang, 2010), aromaticity (Mikutta et al., 2007), functional groups (Swenson et al., 2015, Lu et al., 2010, Liu and Lee, 2006, Kang and Xing, 2008, Ahmat et al., 2015, Aufdenkampe et al., 2001) and DOM source (Satterberg et al., 2003), hence comparisons between different studies can be difficult. However, it is unrealistic to measure all of these characteristics in all studies because they are both expensive and time consuming. For this reason, a classification method based on easily measurable characteristics was developed with DOM categorised as terrigenous 1 (T1) , terrigenous 2 (T2) or Autochthonous (A) (Anderson et al., 2019). DOM T1 is characterised as strongly UV absorbing, younger, more coloured, more reactive terrestrial organic matter. That prone to photooxidation and flocculation, but less susceptible to microbial degradation, typically released from topsoils. Examples of this include lignin and other structural compounds from an upland source. DOM type T2 is weakly UV absorbing, older, less reactive and less coloured terrestrial organic matter. That prone to microbial degradation but less susceptible to photooxidation and flocculation, these compounds can percolate further down soil substrates and can be released from baseflow. Typically derived from arable soils and included manmade DOM such as sewage. Examples of compounds include carbohydrates and proteins. DOM type A is aquatically produced DOM produced via phytoplankton exudation, zooplankton grazing and detritus turnover. These compounds are not susceptible to photo oxidation but are semi labile with a turnover of weeks to months.

In this study, DOM type T1 was collected from the Nant y Brwyn (longitude: -3.802^{o}, latitude: 52.988^{o}), an undisturbed upland peat stream in Snowdonia Wales, and the organic matter T2 sample was collected from a more arable setting the Plas Uchaf reservoir (longitude: -3.546^{o}, latitude: 53.229°), near to St Asaph, Wales. The organic matter A sample came from the phytoplankton *Tetraselmis suecica,* (collection protocol described in section 2.1.1). A suspension of 0.33 gL^{-1} in deionised water was prepared and shaken for 17 hours to allow dissolution of the more soluble organic compounds. All three DOM types were then filtered through GF/C filters, with a nominal pore size of 0.45 µm. Filtering was completed prior to experiments to obtain the dissolved fraction.

Batch experiments of mineral clay fractions were performed to evaluate the difference between true aluminosilicate clays and other minerals of clay size (< 4 µm). Kaolinite and bentonite were used to represent the 1:1 and 2:1 clays, respectively; the non-aluminosilicate clay was represented by Bangor Soil that was collected from Pontbren, near Llanfair Caereinion, Wales. All three minerals were heated to 400°C overnight to remove any native organic matter.

2.3.2 Instrumentation

Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) measurements were performed using a Thermalox 5001.03 from Analytical Science. Solutions were acidified, sparged with oxygen to remove carbonate, and then calibrated with a 7-point calibration curve. Four 40 µL injections were made with an average coefficient of variance of 4 % for carbon and 6 % for nitrogen. Samples above a coefficient of variance of 20 % were repeated. All samples were calibrated using an external calibration curve. The specific electrical conductivity (SEC) was measured with a Jenway 4320 and the pH with a Metrohm Titrando with an Aquatrode +Pt 1000 pH electrode. Anion and cation contents were determined on a Metrohm 930 compact IC flex ionic chromatograph calibrated with a 7-point calibration curve.

Fluorescence Excitation-Emission Matrix (EEM) was used to determine the DOM classifications (Lapworth et al., 2008). A Varian™ Cary Eclipse fluorescence spectrometer was used for the fluorescence analyses. Excitation (Ex) wavelengths were set between 200 and 400 nm with a 5 nm bandwidth and emission (Em) wavelength set between 250 and 500 nm with a 2 nm bandwidth. The scan rate was 9600 nm/min and the PMT voltage was 725 V. One cm path length quartz cells were used. Ultrapure water (ASTM type I reagent grade water, including a UV cracker) was used for the blank samples and to clean the quartz cell between samples. Post processing of the fluorescence data, the blank and the absorbance correction, was carried out using the statistical package, R (R-Team, 2008, Lapworth and Kinniburgh, 2009).

Multivariate techniques are commonly used to evaluate and characterize the complex mixtures of fluorescent DOM (fDOM) fractions in environmental waters. The most common method employed is Parallel Factor Analysis (PARAFAC) (Bro, 1997) and is used in this study. This method decomposes the combined fluorescence signal into individual, distinct modelled components (Bro, 1997, Murphy et al., 2013, Stedmon et al., 2003) . EEM-PARAFAC then models the three-way (excitation, emission, intensity) EEM data using fitting routines to minimise the sum of squares of the residuals (Stedmon and Bro, 2008). The 'DOMFluor v1.7' toolbox(Stedmon and Bro, 2008) was used to undertake this analysis, explore the data set and validate the PARAFAC modelling. A three fDOM component model was validated using independent split-half analysis of the data set following removal of outlier data which had high leverage (Stedmon and Bro, 2008). The inclusion of further components could not be validated, and the three component model explained 99.5% of the variability in the absorbance corrected EEM data. The three components identified were: Component 1 (C1, Ex/Em: 245-380/416-462 nm), component 2 (C2, Ex/Em: 245-345/372-444 nm) and component 3 (C3, Ex/Em: 245-315/314-376 nm). Based on previously reported distributions of Em/Ex these components have been assigned as: C1 humic-like, C2 fulvic-like, C3 tryptophan-like (Coble, 1996, Chen et al., 2003). Other DOM characteristics were investigated through the use of two further indices: (i) the fluorescence index (FI), which is commonly used to differentiate between terrestrial and microbial DOM sources (McKnight et al., 2001), and (ii) the humification index, an indication of humicity, and the condensing of fluorescing molecules (Zsolnay, 2001). This analysis was carried out by Dr Dan Lapworth at the British Geological Survey.

The mineralogy of the solid phases was again determined by X-ray diffraction (XRD) using a Panalytical X'Pert pro diffractometer machine fitted with a Cu X-ray tube, operating at 35 kV, 40 mA utilising automatic slits and a step size of 0.02º 2θ at 1 second/ step. Semi-quantitative analysis was undertaken using a least squares method similar to that used in the Microsoft Excel-based programs RockJock (Eberl, 2003), and FULLPAT (Chipera and Bish, 2002). Surface areas were determined with nitrogen absorbance using the Brunauer-Emmett-Teller (BET) method on a micromeritics 3 flex 3.02 at 77 K

2.3.3 Analysis of starting material

The natural organic matter used in the CEH work detailed in chapter 6 was analysed using dissolved organic carbon and total nitrogen measurements, as well as conductivity, pH together with a number of fluorescence derived indexes. The fluorescence index (FI), which is commonly used to differentiate between terrestrial and microbial DOM sources (McKnight et al., 2001), and (ii) the humification index, an indication of humicity, and the condensing of fluorescing molecules (Zsolnay, 2001). Parallel Factor Analysis (PARAFAC)(Bro, 1997) was used to separate the excitation, emission matrix into 3 components, assigned as: humic-like, fulvic-like and tryptophan-like (Coble, 1996, Chen et al., 2003) whose relative concentrations are presented in

Raman units. These show the differences between the three DOM types (see *Table 2.3*). Fluorescence index shows all are low in microbial organic matter, but variation is consistent with three different sources. The humification index indicates A is the least degraded and T1 is a little more degraded than T2. The EEM results also suggest a differing chemical makeup with different proportion of the three protein types.

Table 2.3. Showing the properties of DOM solutions T1, T2 and A.

Sample	**T1**	**T2**	**A**
DOC/ mgL^{-1}	14.63	14.30	5.8
TDN mgL^{-1}	0.37	1.96	0.57
Specific Electrical conductivity/ µScm^{-1} (salinity/ PSU)	24.5 (0.019)	153.4 (0.076)	24.5 (0.019)
pH	5.65	7.3	6.48
Fluorescence index	1.04	1.23	0.87
Humification index 2	0.92	0.89	0.48
EEM humic Fmax/ RU	3.45	1.87	0.245
EEM Fluvic Fmax/ RU	4.87	3.12	1.11
EEM trypophan Fmax/ RU	0.31	0.20	0.57

Minerals were analysed by XRD to determine composition and BET to determine surface area. The X-ray diffraction (XRD) composition of kaolinite was 72.9% kaolinite, 23.8% illite and 6.3% quartz. For bentonite the XRD composition was 89.1% montmorillonite (swelling clay), 9% albite, 1.9% quartz. Bangor soil XRD composition was 44.6 % illite, 35.3 % quartz, 10 % smectite 8 % albite, 2.1 % chlorite, and a clay sized fraction of 39.9 % ±7.8. The results of BET surface area measurements can be seen in *Table 2.4*.

Table 2.4. Surface area and composition of minerals used in CEH experiments.

Mineral/soil	BET Surface area/ m²/g	XRD composition
Kaolinite	16.3	72.9% kaolinite, 23.8% illite and 6.3% quartz.
Bentonite	12.4	89.1% montmorillonite (swelling clay), 9% albite, 1.9% quartz
Bangor soil	18.3	44.6 % illite, 35.3 % quartz, 10 % smectite 8 % albite, 2.1 % chlorite

2.3.4 Experimental set up

For the incubation experiments, the starting DOM solutions were first adjusted to the required salinity. For riverine samples, no adjustment was required. For marine samples, artificial sea salt made according to (Subov, 1931) was added to give a salinity of 30. These solutions were allowed to stand for 15 minutes before being filtered through GF/C filters with a nominal pore size of 0.45 µm. Three aliquots of this starting solution were set aside to measure $DOC_{initial}$. 30 mL of DOM solution were added to centrifuge tubes containing the appropriate mass of mineral. Tubes were shaken for 2 hours before being filtered through Whatman GF/C filters (0.45 µm) prior to analysis by DOC, giving DOC_{final}. This process is illustrated in *Figure 2.14*. Analysis was generally conducted within 3 hours. In a few instances when this was not possible samples were stored at 4 °C and analysed within 24 hours. Storage at this temperature over these timescales has previously been shown to reduce any degradation to below detectable level (Peacock et al., 2015).

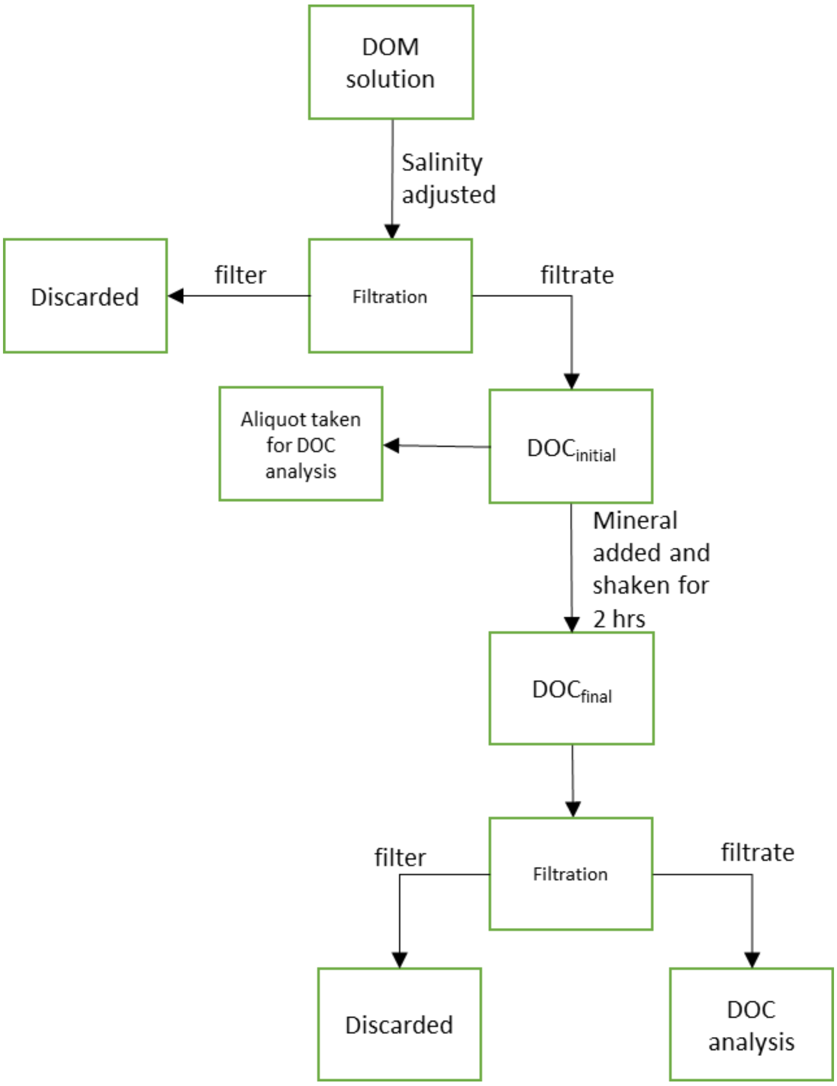


Figure 2.14. Flow diagram of the reaction, separation and analysis process in CEH work.

2.4 Conclusion

This chapter has outlined the methods that were used to investigate organic matter mineral bonding within this study. Sensitivity experiments (*Figure 2.6*, *Figure 2.7* and *Figure 2.13*) indicate that these methods are capable of separating bound and unbound organic matter, including particulate organic matter. These methods also allow a range of organic matter, minerals and conditions to be investigated. In addition, the starting materials were successfully characterised, demonstrating that they represent a variety of organic matter and mineral source representative of the marine environment.

Chapter 3 Importance of Organic matter type on the extent of organic matter-mineral sorption

3.1 Introduction

The aim of this study is to investigate the effect of functional group and molecular weight on organic matter- mineral interactions under different organic matter-mineral ratios.

In marine sediments, the burial of organic matter is a major link between the active surficial carbon pools in the ocean, atmosphere and land and the pools that cycle on geological ($10^{\wedge 5}$) time scales (i.e., sedimentary rocks), playing a role in controlling CO_2 and O_2. The majority of organic matter preserved within sediments is intimately associated to the mineral matrix through sorption on clay minerals and metal oxides (Keil and Hedges, 1993). Organic matter preservation is dependent on its type (Kang and Xing, 2008, Swenson et al., 2015, Aufdenkampe et al., 2001, Lu et al., 2010, Ahmat et al., 2015, Newcomb et al., 2017), the strength of organic matter-mineral interactions, and the time scales involved (Henrichs, 1995). Previous studies have either concentrated on a specific subset of organic compounds (such as humic acids) or on natural samples of organic matter, which contain a wider range of functional groups. The analytical method used to identify organic matter type can be biased towards certain organic matter types, for example GC-MS will only reveal compounds that are sufficiently volatile, i.e., the compounds that are observed to be binding may not be the only ones that are binding. In addition, with natural organic matter samples, the amount of organic matter of a specific type that binds is also influenced by its abundance in the environment (Ahmat et al., 2015). This study adopted an approach that included a range of organic compounds representing different functional groups added to minerals in equimolar quantities to isolate the effect of abundance on binding preferences.

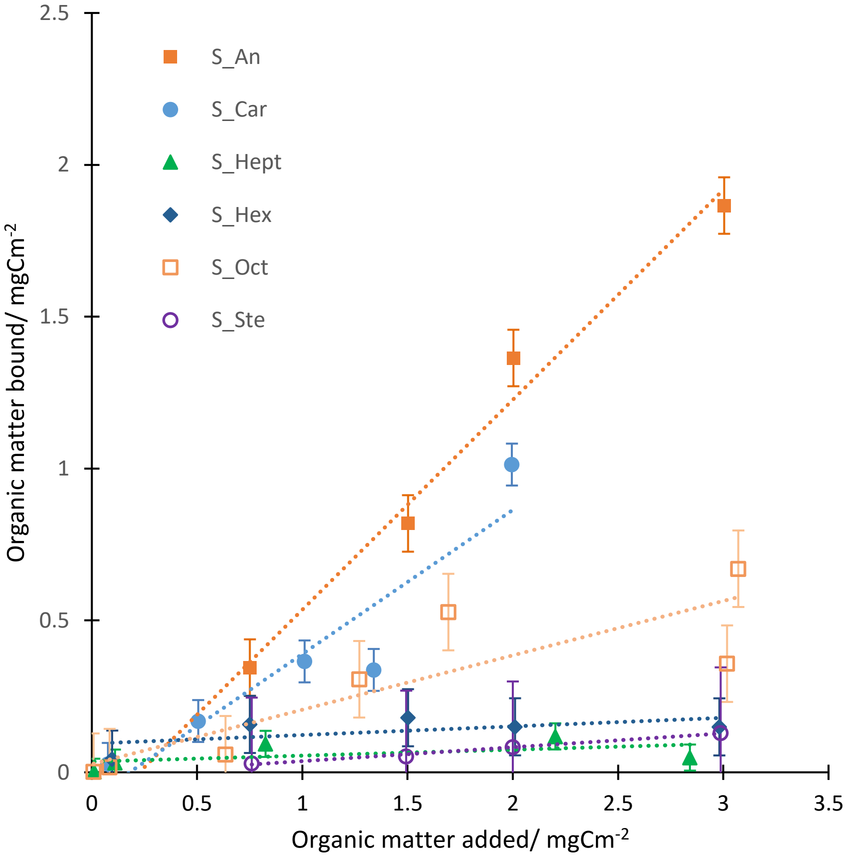
3.2 Method

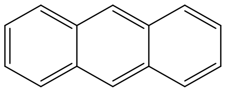
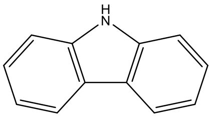
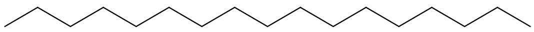
The methodology used in this investigation is detailed in Chapter 2. In brief the compounds in *Table 2.1* were added, both individually and in combination, to a suspension of kaolinite. Sorption was monitored by isolating the kaolinite using centrifugation. The organic matter associated with the kaolinite was extracted using solvent extraction and analysed by GC-MS.

3.3 Results and discussion

3.3.1 Individual compounds

Initial experiments concentrated on six compounds: anthracene, carbazole, heptadecane, hexadecanol, octadecanamide and stearic acid, representing the organic matter classes: aromatic, aromatic and nitrogen-containing, alkane, alcohol, amide and fatty acid, respectively. When added to kaolinite individually, the results plot differently per compound (*Figure 3.1*).



Compound	Formula	Line of best fit	R^2 value
Anthracene ■		y = 0.6912x - 0.1559	0.98
Carbazole ●		y = 0.4745x - 0.0851	0.87
Heptadecane ▲		y = 0.0197x + 0.0352	0.28

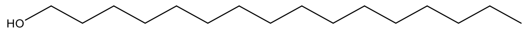
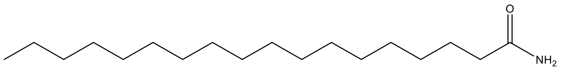
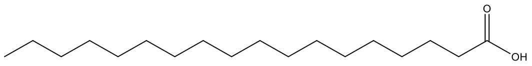
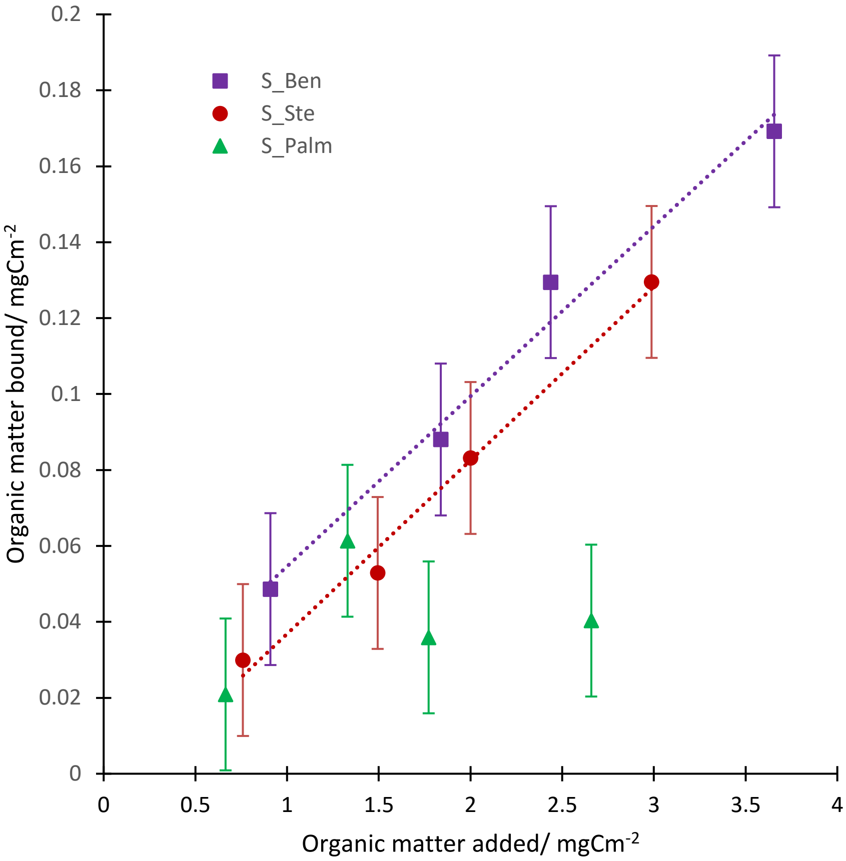
Hexadecanol ◆		y = 0.0283x + 0.0946	0.35
Octadecanamide □		y = 0.179x + 0.027	0.75
Stearic acid ○		y = 0.0457x - 0.0089	0.90

Figure 3.1. Sorption of individual compounds to kaolinite. Units in mg of carbon per metre squared of mineral surface. An-Anthracen, Car-Carbazole, Hept-Heptadecane, Hex-Hexadecanol, Oct-Octadecanamide and Ste-Stearic acid.

The greatest sorption is shown by the two aromatic compounds; anthracene and carbazole. Octadecanamide shows intermediary sorption; hexadecanol, stearic acid and heptadecane show the poorest sorption. This result differed from previous studies which report preferential sorption with polar compounds, particularly those containing nitrogen (Ahmat et al., 2015, Kang and Xing, 2008, Newcomb et al., 2017, Aufdenkampe et al., 2001). Poor sorption of heptadecane is consistent with previous studies that show poor interactions of alkanes with mineral surfaces (Newcomb et al., 2017, Lu et al., 2010). The tendency for greater sorption of nitrogen-containing compounds explains the greater sorption of octadecanamide than hexadecanol, stearic acid and heptadecane. However, this effect is not observed in the aromatic compounds as the nitrogen-containing carbazole shows poorer sorption than anthracene. This indicates that the aromatic nature of these compounds may be of greater importance than the presence of the nitrogen in the organic matter. Although this strong preference for aromatic compounds has not been reported previously, Swenson et al. (2015) found some preference for aromatic compounds. However greater sorption was shown by phosphate and dicarbonyl groups (Swenson et al., 2015). This difference may result from a difference in the mineral used in this study (e.g., Swenson used goethite as opposed to kaolinite); alternatively it may reflect a greater abundance of phosphate and dicarbonyl compounds in the bacterial metabolites used by Swenson et al.

A low concentration or complete lack of aromatic compounds in previous studies, may explain why they have rarely been found to be important. A number of studies did not use aromatic compounds (Lu et al., 2010, Newcomb et al., 2017), and others had only a low proportion of aromatic compounds (Swenson et al., 2015, Ahmat et al., 2015, Aufdenkampe et al., 2001). This is partially due to aromatic compounds constituting a small proportion of naturally occurring organic matter (Hedges et al., 2001), although aromatic compounds are an important component of humic acids (Kang and Xing, 2005). However, Wang and Xing found that it was aliphatic and not aromatic humic acids that bound more readily to clay minerals (Wang and Xing, 2005). This could be due to a difference in size between the small compounds used here and macromolecules (e.g., humic acids). The increased bulk of aromatic humic compounds may make it harder for them to approach in the mineral surfaces. A final consideration is that in the current study compounds were exposed to the mineral individually without competition from other compound types. This may explain some of the differences noted. In order to investigate this possibility later experiments exposed the six compounds to the mineral surface in a combined fashion (i.e., with all six compounds present in the same solution; see Section 3.3.2).

Previous studies observed that molecular weight, as well as functional groups, can impact organic matter-mineral binding (Arnarson and Keil, 2000). To further investigate this effect, sorption of three fatty acids of different chain lengths was explored. The use of fatty acids with differing chain length allows for comparison of compounds which are of differing molecular weight, but similar functionality. This removes the effect of higher molecular weight compounds often containing a larger number of functional groups within natural organic matter. The fatty acids used were behenic acid (molar mass: 340.58 gmol^{-1}, $C_{22}H_{44}O_2$), stearic acid (molar mass: 284.48 gmol^{-1} $C_{18}H_{36}O_2$) and palmitic acid (molar mass: 256.43 gmol^{-1} $C_{16}H_{32}O_2$). Results are reported in *Figure 3.2*. All three compounds show increased sorption as higher concentrations are added, with a linear response being shown by behenic and stearic acid. Palmitic acid sorption appears to level off at the highest concentrations. For a given amount of each compound added, the greatest sorption is shown by behenic acid, followed by stearic acid and then palmitic acid. At the lower concentrations, this difference in sorption is within experimental error for all three compounds but at the higher concentrations only the difference between behenic and stearic acid are within experimental error.



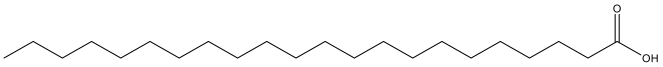
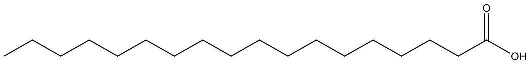
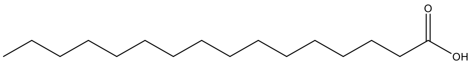
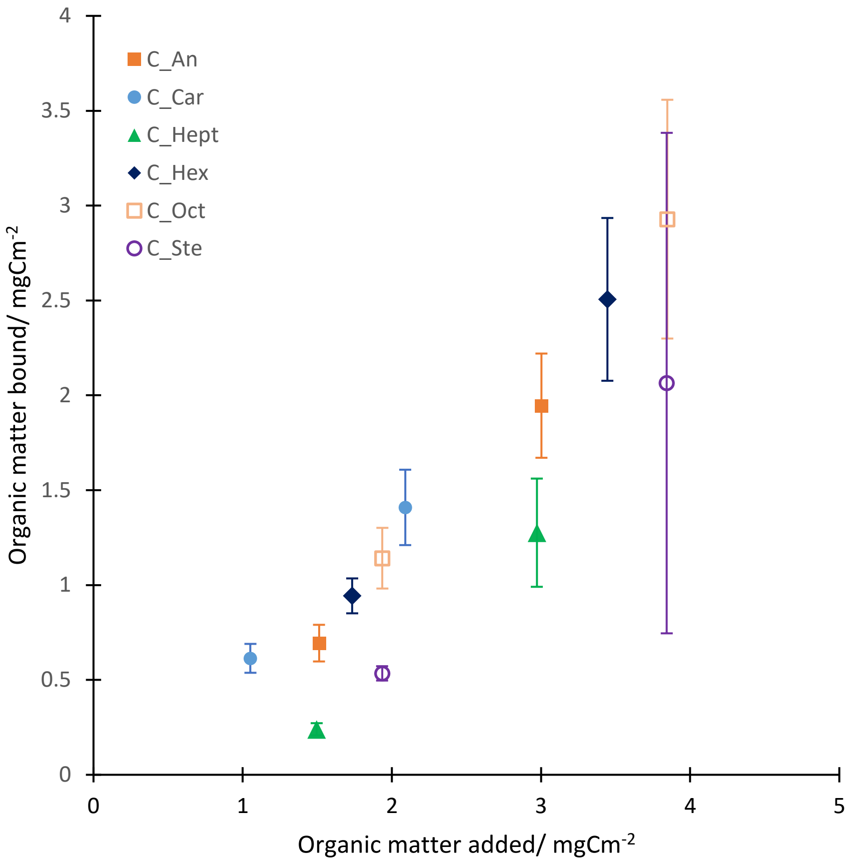
Compound	Formula	Line of best fit	R^2 value
Behenic acid ■		y = 0.0448x + 0.0098	0.98
Stearic acid ●		y = 0.0457x - 0.0089	0.99
Palmitic acid ▲		Poor correlation	

Figure 3.2. Sorption of fatty acids to kaolinite in units of mg of carbon per metre squared of mineral surface. Ben-behenic acid, Palm-Palmitic acid, Ste-stearic acid.

The greatest sorption shown by behenic acid, followed by stearic acid and palmitic acid showing the least sorption suggests that the increased sorption previously noted for higher molecular weight compounds likely results from factors additional to increased functional groups. The increased sorption may be caused by the larger fatty acids being more hydrophobic or because higher molecular weight compounds are able to form stronger Van De Waal interactions. The nature of interactions between the organic matter and the mineral is investigated further in Chapter 4.

3.3.2 Combined compounds

In combined experiments all six compounds (anthracene, carbazole, heptadecane, hexadecanol, stearic acid and octadecanamide) were present in equimolar quantities when exposed to kaolinite. This was carried out at two different organic matter concentrations with three repeats at each concentration. *Figure 3.3* shows how the amount of organic matter sorbed increases as more organic matter is added, as *Figure 3.1* did for the single compound experiments. This shows that the variation between the six compounds is much reduced in the combined experiments compared to the single compound experiments. *Figure 3.4* shows the average percentage of organic matter added that binds to kaolinite for the six compounds in both the combined and single compound experiments. This shows that for all the compounds, except anthracene, much greater sorption is achieved in the combined experiments than in the single compound experiments. Whilst anthracene shows similar sorption in both experiments.



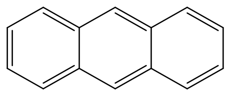
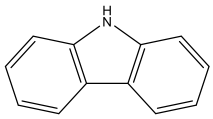
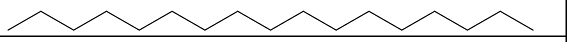
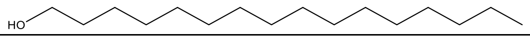
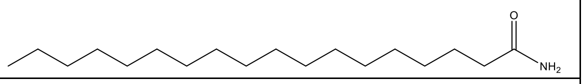
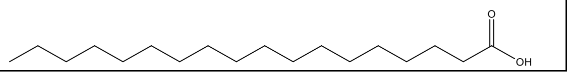
Compound	Formula
Anthracene ■	
Carbazole ●	
Heptadecane ▲	
Hexadecanol ◆	
Octadecanamide □	
Stearic acid ○	

Figure 3.3. Sorption of competing compounds to kaolinite. An-Anthracene, Car-Carbazole, Hept-Heptadecane, Hex-Hexadecanol, Oct-Octadecanamide and Ste-Stearic.

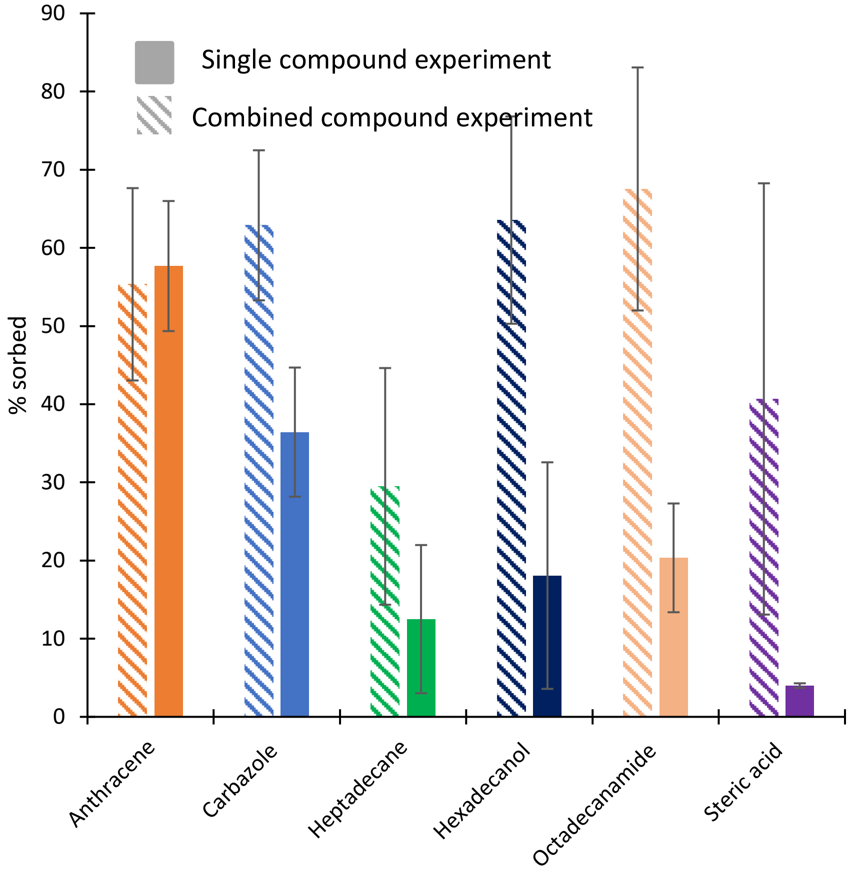
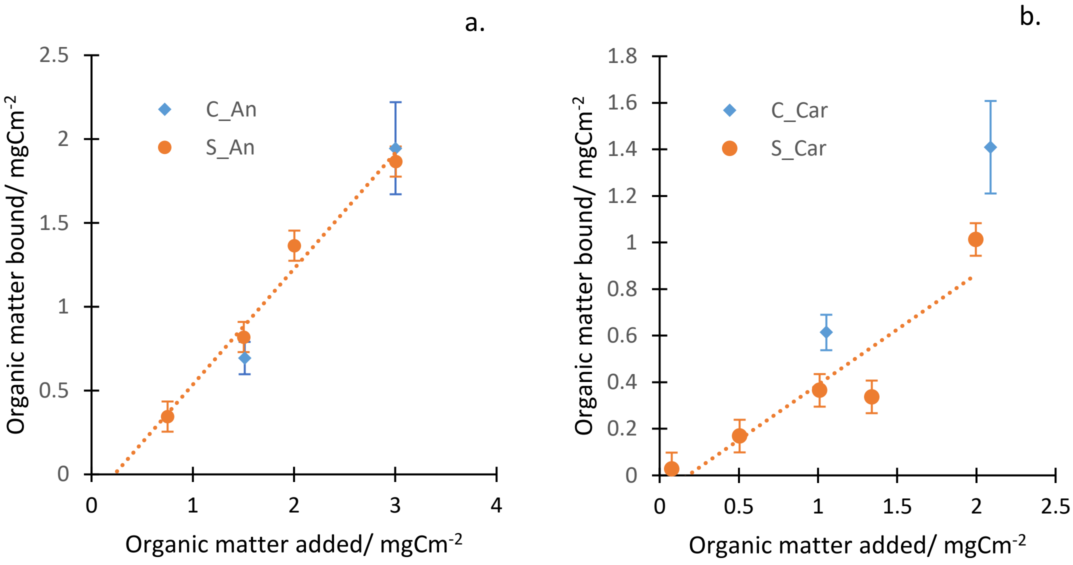


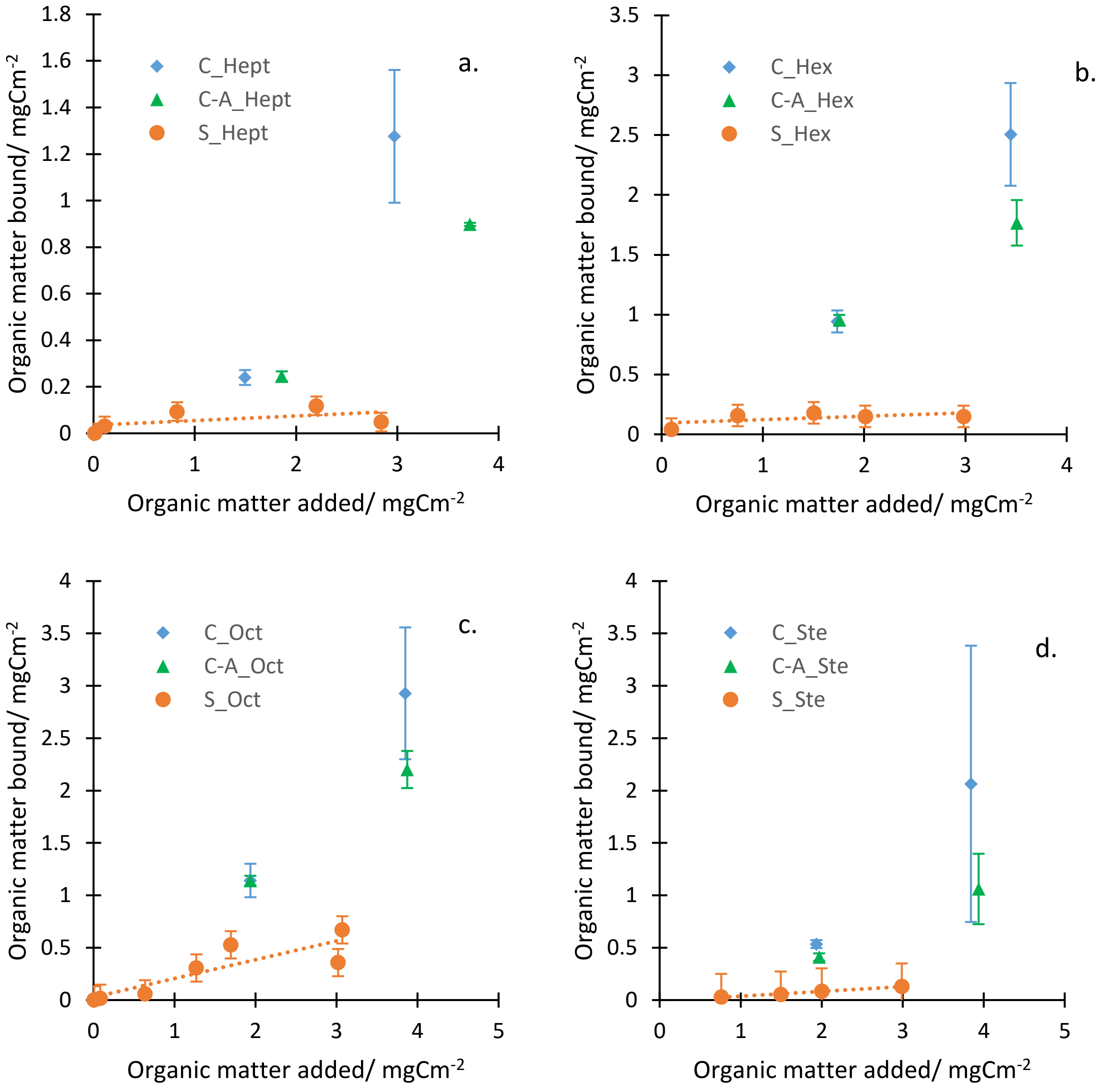
Figure 3.4 showing the average percentage of added organic matter sorbing to kaolinite

This result implies that the presence of multiple types of organic matter promotes sorption, rather than the different types competing. Secondly the minimal variation between the sorption of all six compounds should be noted. This differs from the single compound experiments where the two aromatic compounds showed notably greater sorption. Stearic acid and heptadecane show a slightly lower sorption, but the variation is less than in the single compound results. A possible explanation for this observation is that the aromatic compounds are binding to the clay surface and the non-aromatic compounds are binding to the aromatic compounds. As can be seen in *Figure 3.5*, the difference in the amount of binding shown by the aromatic compounds in the combined experiments and the single compound experiments is minimal. To test this, the sorption experiments were repeated with only the four non-aromatic compounds (*Figure 3.6*). *Figure 3.7* compares the average percentage of organic matter added which sorbes to the mineral kaolinite for the single combined and combined-aromatic experiments.



a. Anthracene	Single ●	Combined ◆		b. carbazole	Single ●	Combined ◆

Figure 3.5 a) and b). Sorption of aromatic compounds in the presence and absence of competing molecules. Units are mg of carbon per metre squared of mineral surface. An-Anthracene, Car-Carbazole, S-single, compound present in isolation, C-combined, anthracene, carbazole, heptadecane, hexadecanol, octadecanamide and stearic acid all present in solution.



a. Heptadecane	Single ●	Combined ◆	Combined- aromatic▲		b. Hexadecanol	Single ●	Combined ◆	Combined- aromatic▲
c. Octadecanamide	Single ●	Combined ◆	Combined- aromatic▲		d. Steric acid	Single ●	Combined ◆	Combined- aromatic▲

Figure 3.6 a, b, c and d. Sorption of non-aromatic compounds to kaolinite in the presence and absence of competing molecules. Units are in mg of carbon per metre squared of mineral surface. Hept-Heptadecane, Hex-Hexadecanol, Oct-Octadecanamide, Ste-Stearic acid, S-single, compound present in isolation, C-combinded, anthracene, carbazole, heptadecane, hexadecanol, octadecanamide and stearic acid all present in solution.C-Combined minus aromatic, , heptadecane, hexadecanol, octadecanamide and stearic acid all present in solution.

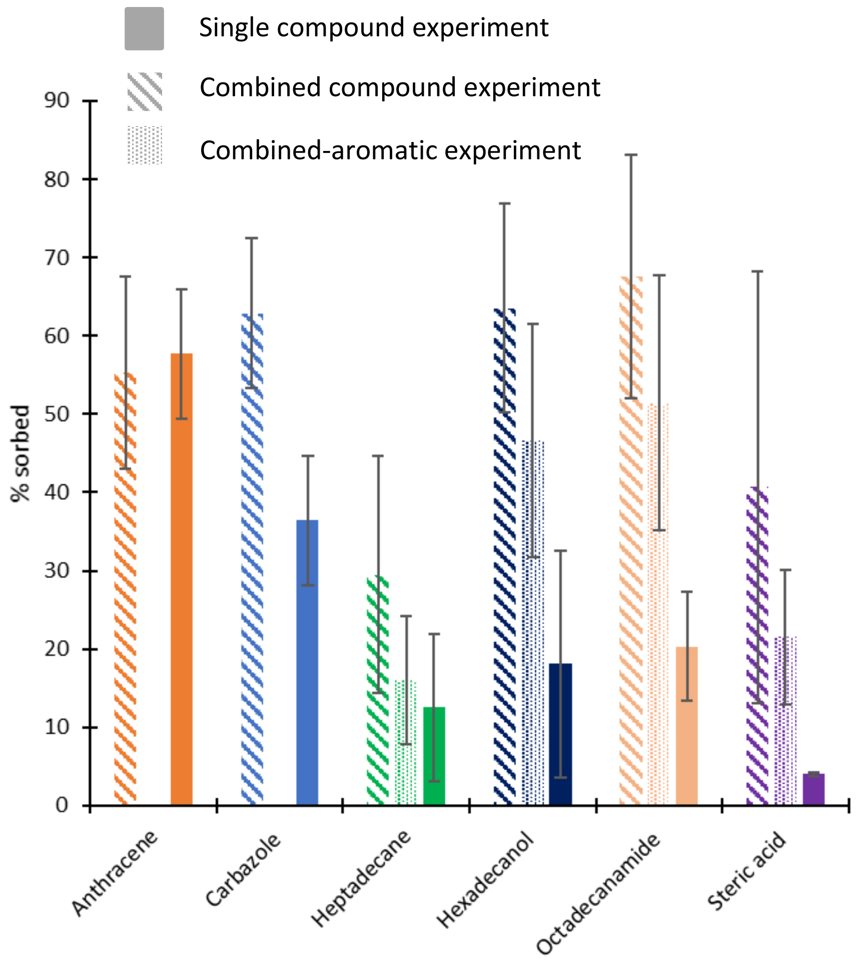
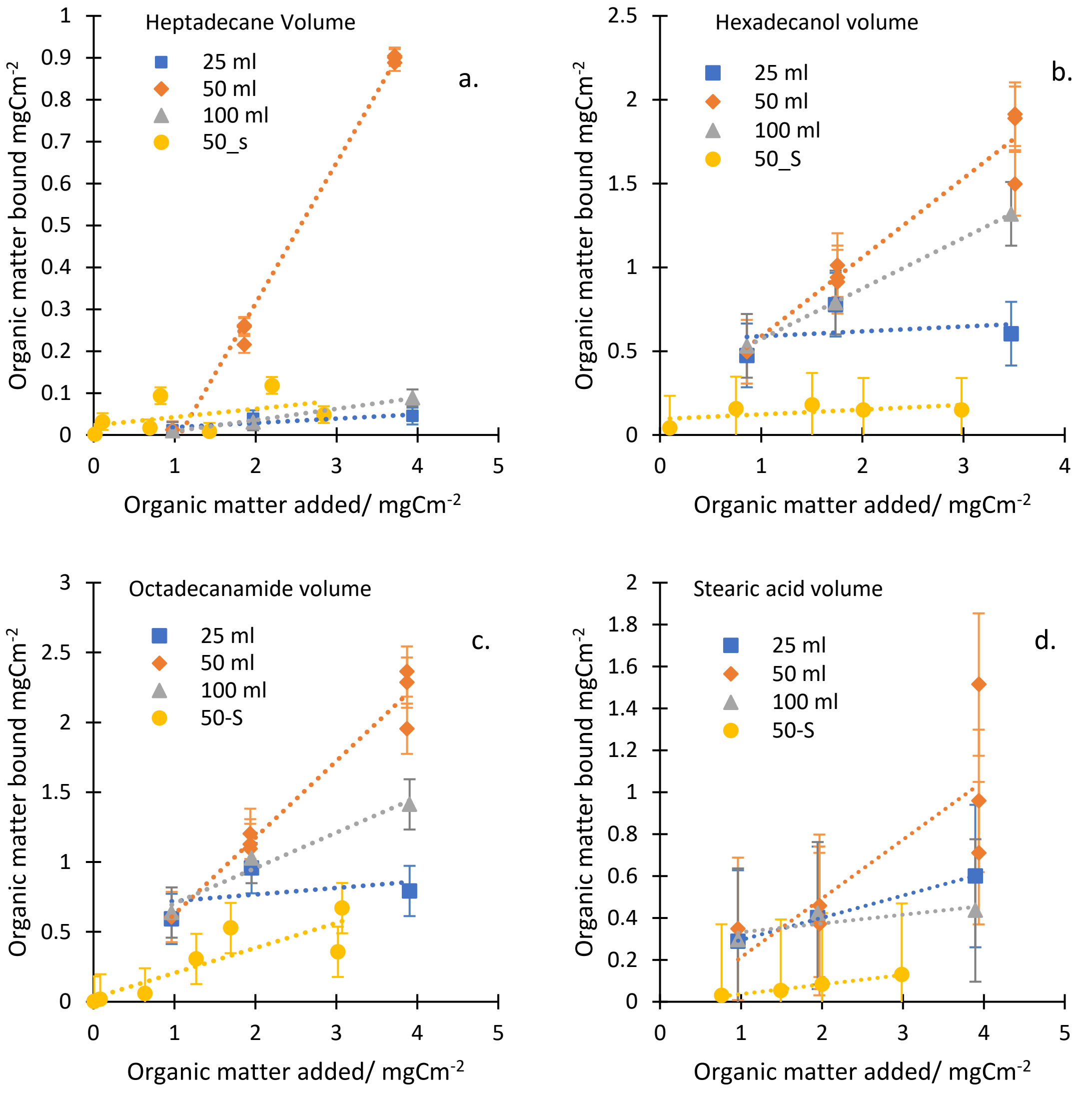


Figure 3.7 showing the average percentage of added organic matter sorbing to kaolinite

The absence of aromatic compounds results in reduced sorption, however sorption is still higher than compounds sorbed in isolation. The combined results in absence of aromatics show greater similarity to the combined with aromatic results than to the single compound data. These results suggest that the presence of the aromatic compounds alone is not the cause of the increased sorption. A possible explanation is that the presence of additional organic matter does not directly cause increased binding by one type binding to the mineral and another binding to that. Rather, it may be purely a solubility effect. The increased overall concentration of compounds in solution may be causing the compounds to move to the sorbed phase. This effect will be increased by these compounds being only sparingly soluble in water. To test this hypothesis, combined without aromatic experiments were performed at different volumes. This involved keeping the organic matter: mineral ratio the same whilst varying the volume of seawater added, in order to change the concentration of the organic matter in solution. If the increased sorption is caused by decreased solubility, then there should be greater sorption seen at lower volumes. Results of this experiment can be seen in *Figure 3.8*.



a. Heptadecane	Combined 25 mL ■	Combined 50 mL ◆	Combined 100 mL ▲	Single 100 mL ●
b. Hexadecanol	Combined 25 mL ■	Combined 50 mL ◆	Combined 100 mL ▲	Single 100 mL ●
c. octadecanamide	Combined 25 mL ■	Combined 50 mL ◆	Combined 100 mL ▲	Single 100 mL ●
d. stearic acid	Combined 25 mL ■	Combined 50 mL ◆	Combined 100 mL ▲	Single 100 mL ●

Figure 3.8 a, b, c and d. Effect of volume on degree of sorption in four non-aromatic compounds when added competitively. Sorption when compounds added singly added for comparison.

All compounds at all volumes show a positive correlation between the amount of organic matter added and the amount of organic matter bound. All four compounds show the greatest sorption where the experimental volume is 50 mL. In the heptadecane this sorption is much greater than the sorption shown at 25 and 100 mL which show a greater resemblance to the single compound results. This suggests there may be some experimental errors in the data. Possibly the volatile nature of heptadecane resulted in partial evaporation in the 100mL and 25mL samples during the extraction. Alternatively, it may be that the 50 mL sample was contaminated at some point resulting in a higher concentration. In Hexadecanol the second greatest sorption is shown in the 100 mL experiment with 25 mL showing the least sorption of the 3 volumes but greater sorption than hexadecanol in the single compound experiments. This pattern is repeated for the octadecanamide experiment. However, in the stearic acid experiment 25 mL and 100 mL show similar responses but with a slightly greater sorption in 25 mL than 100. Overall, lower volumes do not show increased sorption. This suggests that increased sorption in the combined samples is not due only to the increased concentration making sorption more favourable, strongly suggesting that in the combined samples, the six compounds are actively promoting binding and not competing with each other to bind to the mineral. This is consistent with previous studies that have suggested that organic matter within marine sediments is preserved as part of a complex 3D structure (Liu and Lee, 2006). This structure has been demonstrated to be easily affected by environmental conditions, such as drying and rewetting. This 3D structure may also explain the stronger sorption of hydrophobic compounds when hydrophilic compounds have previously been found to be preferable.

In order to further investigate whether a 3D structure is responsible for the increased sorption shown in the combined experiments the percentage of organic matter sorbed at different organic matter concentrations was compared in *Figure 3.9* and *Figure 3.10*. A flat line or a line with a positive gradient indicates that the organic matter binding sites on the mineral are not reaching saturation because as more organic matter is added the same or a higher percentage of organic matter is able to bind. However, a negative gradient suggest that saturation has been reached because when more organic matter is added the same percentage is no longer able to bind. In the single compound experiments a negative gradient can be seen in heptadecane, octadecanamide and hexadecanol suggesting that these are reaching saturation at the higher concentrations. Whereas the remaining three compounds show a positive gradient, suggesting saturation has not been reached. In the combined experiments all six compounds show a positive gradient meaning saturation is not reached. This implies that the hexadecanol, octadecanamide and heptadecane are binding to different sites in the combined experiments than in the single experiments, this would be consistent with a 3D structure in which some compounds bind to the mineral and others bind to those compounds.

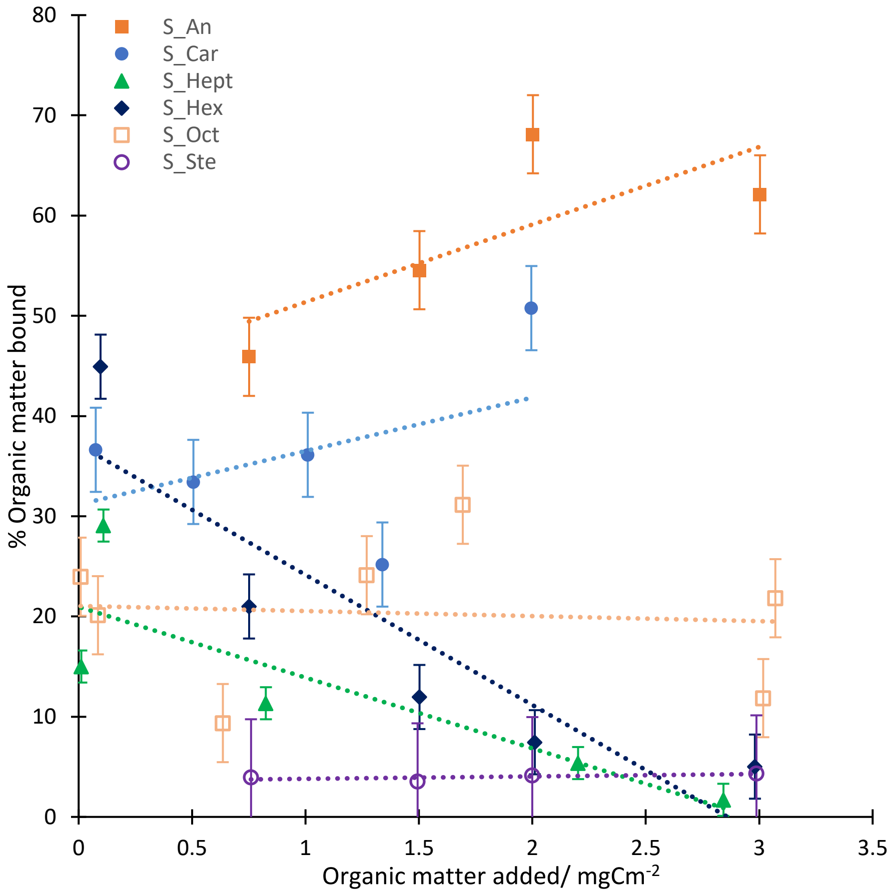
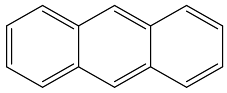
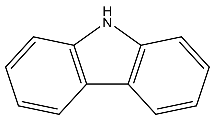
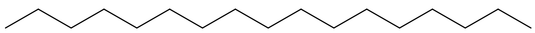
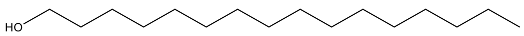
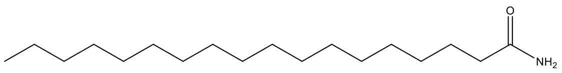
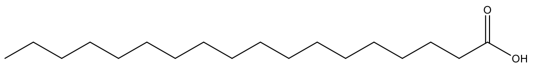


Figure 3.9 showing the percentage of organic matter sorbed for different amounts of organic matter added in single compound experiments

Compound	Formula	Gradient
Anthracene ■		7.7
Carbazole ●		5.3
Heptadecane ▲		-7.1
Hexadecanol ◆		-13.0
Octadecanamide □		-0.5
Stearic acid ○		0.2

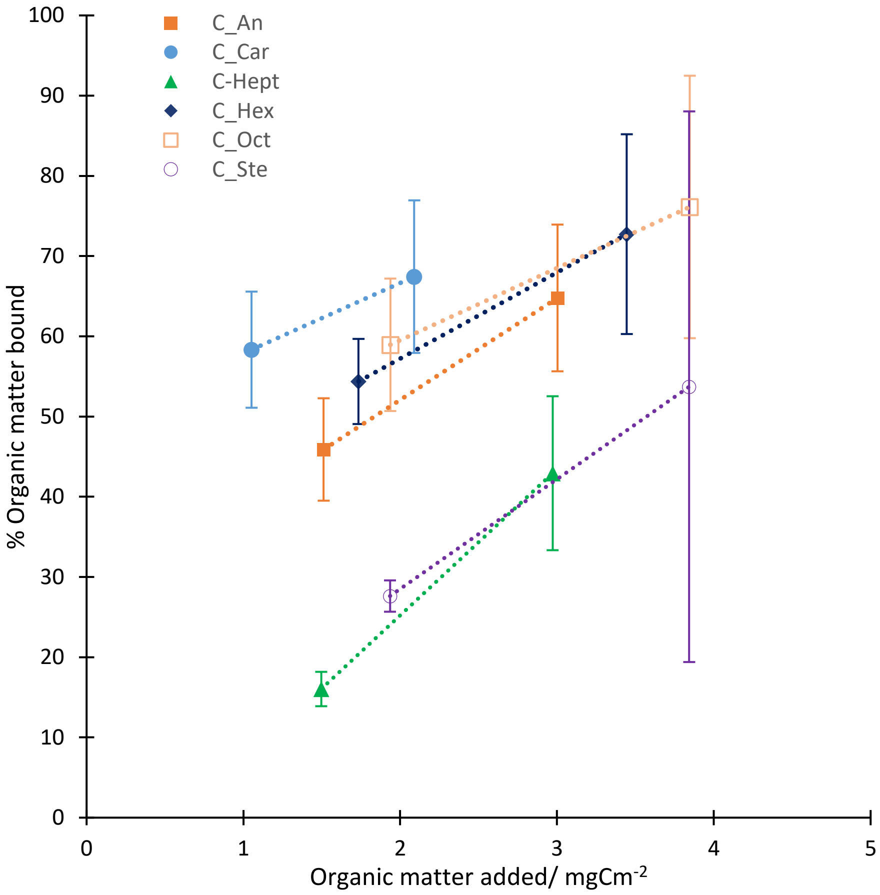
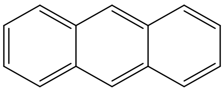
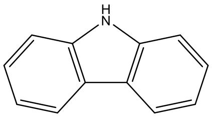
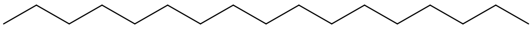
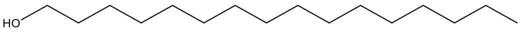
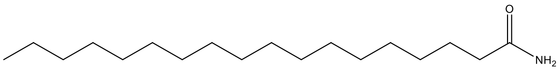
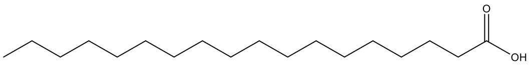


Figure 3.10 showing the percentage of organic matter sorbed for different amounts of organic matter added in combined compound experiments.

Compound	Formula	Gradient
Anthracene ■		12.7
Carbazole ●		8.8
Heptadecane ▲		18.2
Hexadecanol ◆		10.7
Octadecanamide □		9.0
Stearic acid ○		13.7

The promotion of sorption by the presence of a wide range of organic compounds may explain why previous studies, on a more limited range of organic compounds have generally found a lower organic matter-mineral ratio than that observed in natural sediments (Mayer, 1994a, Mayer et al., 1988, Arnarson and Keil, 2000, Drouin et al., 2010). Indeed the overall organic matter mineral ratio achieved in the combined experiments is 12.14 $mgCm^{-2}$ which is almost ten times the 1.5 $mgCm^{-2}$, which is typically found in natural samples (Mayer et al., 1985). There are two likely causes. Firstly, this experiment had a relatively short incubation time and there will have been minimal bacterial degradation of the organic matter mineral complexes as shown in *Figure 2.8*. Both sorption to and aggregation with minerals has been shown to reduce microbial degradation of organic matter (Arnarson and Keil, 2005, Ding and Henrichs, 2002). This is because both processes make the organic matter physically inaccessible to microbes and their enzymes, however if this organic matter is weakly or reversibly bound the organic matter will be able to desorb and be degraded (Saidy et al., 2015). The strength of the organic matter-mineral interactions in this study was not determined meaning that it is possible that under natural conditions a portion of the organic matter bound in these experiments would desorb and be degraded. Secondly, because of the aim to untangle the effects of availability and interaction strength the compounds, those compounds present are not in their natural proportions. In this experiment the proportion of aromatic compounds, which were found to bind most readily, was higher than in natural samples, whereas compounds which were found to bind less readily, such as alkanes and fatty acids are generally more common.

3.4 Conclusion

This study demonstrates that organic matter type is an important factor in determining the amount of sorption to the mineral kaolinite. Sorption of individual compounds allowed investigation into the extent these compounds bound in isolation without factors such as abundance and competition. Aromatic compounds were found to show the greatest sorption, followed by nitrogen-containing octadecanamide. As a results aromatic compounds may be preferentially preserved within marine sediments and aromatic concentrations found in marine sediments may not be indicative of original marine concentrations. Preference for higher molecular weight compounds is caused by factors other than increased functional groups. When the compounds were exposed to the mineral competitively, in equimolar proportions, binding of organic matter of different types is complementary rather than competitive. This suggests that organic matter preservation within minerals is via the formation of 3D structures that include organic matter binding to both minerals and to other organic matter. Thus, the nature of both the mineral and the organic matter already present in sediments should affect interactions with any further organic matter in the environment. Therefore, the preservation of organic matter will be affected not only by its own nature and that of the mineral it is binding to, but also by the nature of any organic matter present at the point of sorption.

Chapter 4 Mechanism of organic matter mineral bonding

4.1 Introduction

Organic matter (OM) describes a diverse continuum of organic compounds many of which hold a great deal of information about the life that formed them. These compounds are widely variable in composition and in properties, such as their inherent stabilities and turnover rates during the processes of sedimentation, diagenesis, and lithification. The stability, cycling, and preservation of OM in sediments can be enhanced by the formation of various organic-mineral interactions between OM particles and the surface of minerals (Henrichs, 1995). Six main mechanisms are important to these interactions: ligand exchange, cation bridging, anion exchange, cation exchange, Van der Waals interactions and hydrophobic effects (Arnarson and Keil, 2000). Ligand exchange is the strongest of these interactions and involves the replacement of a hydroxyl group on the mineral surface with the OH group of an organic compound, such as an alcohol or fatty acid (Davis, 1982, Gu et al., 1995). Cation bridging involves electrostatic interactions between the negative surface on clays and negatively charged organic matter via solution cations, which may still be hydrated, thus resulting in the formation of hydrogen bonds (Greenland, 1971). Anion and cation exchange entail the replacement of inorganic ions on the mineral surface with organic species (Greenland, 1971, Wang and Lee, 1993). Van der Waals interactions are weak, short range inter-molecular interactions that are stronger in larger molecules with more non-valence electrons (Rashid et al., 1972, Preston and Riley, 1982). Hydrophobic interactions are purely entropy driven and involve nonpolar molecules being absorbed onto the mineral surfaces from the water (Delle Site, 2001).

To investigate the contributions of these mechanisms, different solution conditions have been employed to promote or inhibit a selection of the above mechanisms. These experiments have been carried out for a variety of different natural materials. Organic matter (OM) extracted from porewater with montmorillonite (Arnarson and Keil, 2000); humic acids with montmorillonite and kaolinite (Feng et al., 2005); and soil organic matter with goethite, pyrophyllite and vermiculite (Mikutta et al., 2007). These studies suggest that ligand exchange, cation bridging, and Van der Waals interactions are important in organic matter-mineral interactions. It remains unclear however, whether the different mechanisms have been promoted by differences in the organic molecules or by difference in the minerals to which they bind. To better understand these mechanisms, the current study examined the binding of six model compounds (anthracene, carbazole, heptadecane, hexadecanol, octadecanamide and stearic acid) to kaolinite, one of the most ubiquitous clay minerals in marine sediments (Porrenga, 1967).

4.2 Material and Methods

Adsorption experiments were carried out as detailed in Chapter 2. In brief the compounds in *Table 2.1* were added individually to a suspension of kaolinite and sorption was monitored. Kaolinite was isolated by centrifugation, extracted and the extract analysed by GC-MS. Baseline experiments were carried out in artificial seawater created according to Subov (1931), ionic strength 0.5, at 20°C and pH 9. Conditions were varied to investigate the different mechanisms as follows. Ionic strength was varied from 0.1- 0.5; lower ionic strength increases the size of the double layer around the clay mineral making it harder for molecules to approach thus reducing Van der Waals interactions. However, the reduction in competing ions means that anion and cation exchange can be promoted by reduced ionic strength. pH was varied from 3 to 9 to allow investigation of hydrophobic interactions, which are promoted in acid molecules at lower pH values because they become protonated and less charged. However, the picture is complicated by the minerals' pH dependent charge. The ionic composition was also varied at a marine ionic strength, with artificial sea water being replaced by a $CaCl_2$ solution, a Na_2SO_4 solution and a NaCl solution. $CaCl_2$ solution was used to promote cation bridging as the 2+ Ca ions are more favourable than 1+ Na. Na_2SO_4 solution was used to inhibit ligand exchange as the SO_4^{2-} ions can outcompete organic ions. NaCl solution was used to provide a background as neither Na^+ nor Cl^- should impact the binding mechanism. Finally, the sorption isotherms were repeated at 11°C to enable an estimate of the enthalpy of bonding. This was done by regression on $C_{dissolved}$ versus C_{sorbed} at equilibrium to give the equilibrium constant in accordance with Freundlich constant partition model *Equation 4.1*. The negative of the natural log of this equilibrium constant was then plotted against the reciprocal of the temperature in Kelvin allowing the enthalpy to be calculated from the gradient, in accordance with the Van't Hoff equation *Equation 4.2*. Initial organic matter concentrations were unchanged for the ionic composition, ionic strength and pH experiments, but were varied in the temperature experiments to investigate K_{eq}.

Equation 4.1

$$C_{adsorbed} = K_{eq} C_{dissolved}$$

Equation 4.2

$$\frac{dlnK_{eq}}{dT} = \frac{\Delta H}{RT^2}$$

4.3 Results and discussion

4.3.1 Ionic composition

Ionic composition data can be used to determine whether ligand exchange or cation bridging are important bonding mechanisms in the bonding of different organic compounds to kaolinite. Na_2SO_4 inhibits ligand exchange as the SO_4^{2-} ions can out compete organic ions, meaning that decreased sorption in the Na_2SO_4 solution can indicate ligand exchange as an important mechanism. $CaCl_2$ promotes cation bridging as the 2+ Ca ions are more favourable than 1+ Na, meaning increased sorption with $CaCl_2$ can indicate cation bridging is an important mechanism.

The effect of different ionic compositions on anthracene is shown in *Figure 4.1*. Anthracene shows greatest sorption in Na_2SO_4, followed by NaCl and $CaCl_2$ showing very similar sorption to NaCl. This suggests that neither ligand exchange nor cation bridging are important mechanisms for anthracene. This is because for ligand exchange it would be expected that Na_2SO_4 would decrease sorption, and for cation bridging $CaCl_2$ should increase sorption. Neither of which is seen here.

In carbazole (*Figure 4.2*) the greatest sorption is seen in $CaCl_2$ followed by NaCl with the least sorption seen in Na_2SO_4. Although the difference is minimal, this is consistent with ligand exchange and cation bridging, the decreased sorption with Na_2SO_4 supporting ligand exchange and the increased sorption with $CaCl_2$ supporting cation bridging. However, as carbazole is uncharged, cation bridging is an unlikely mechanism. Aromatic compounds are able to act as ligands using their aromatic electrons to donate electron density to metal ions, meaning ligand exchange is a possible mechanism.

Heptadecane (*Figure 4.3*) shows greatest sorption in Na_2SO_4, followed by NaCl with $CaCl_2$ showing the least sorption, indicating that neither cation bridging, nor ligand exchange are important in heptadecane binding to kaolinite. As in anthracene, the expected decrease in sorption with Na_2SO_4 for ligand exchange and the increase with $CaCl_2$ if cation bridging was important are not seen.

Hexadecanol (*Figure 4.4*) shows the same pattern as anthracene and heptadecane with greatest sorption in Na_2SO_4, followed by NaCl, followed by $CaCl_2$. Implying that as in these two compounds neither ligand exchange nor cation bridging are important mechanisms in the binding of hexadecanol to kaolinite.

In octadecanamide (*Figure 4.5*) greatest sorption is shown in NaCl, then Na_2SO_4, with $CaCl_2$ showing the least sorption. The decreased sorption seen with Na_2SO_4, suggests some ligand exchange may be present although the reduction relative to NaCl is within experimental error. Cation bridging is not an important mechanism as $CaCl_2$ shows reduced sorption.

Stearic acid (*Figure 4.6*) shows the greatest sorption in Na_2SO_4, followed by NaCl and $CaCl_2$. As seen in anthracene heptadecane and hexadecanol, as in these three compounds this suggests that neither ligand exchange nor cation bridging are important mechanism in stearic acid.

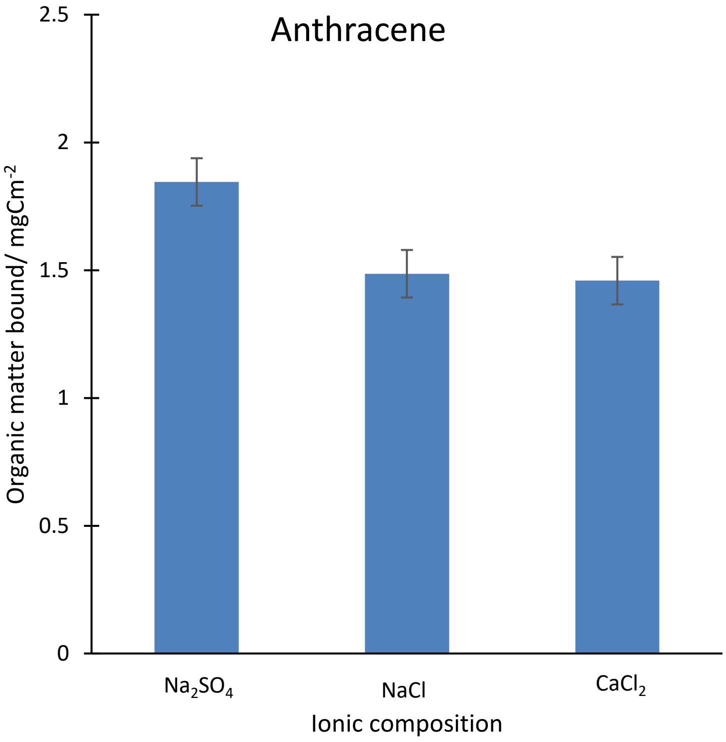


Figure 4.1. Sorption of anthracene to kaolinite in solutions of different ionic compositions.

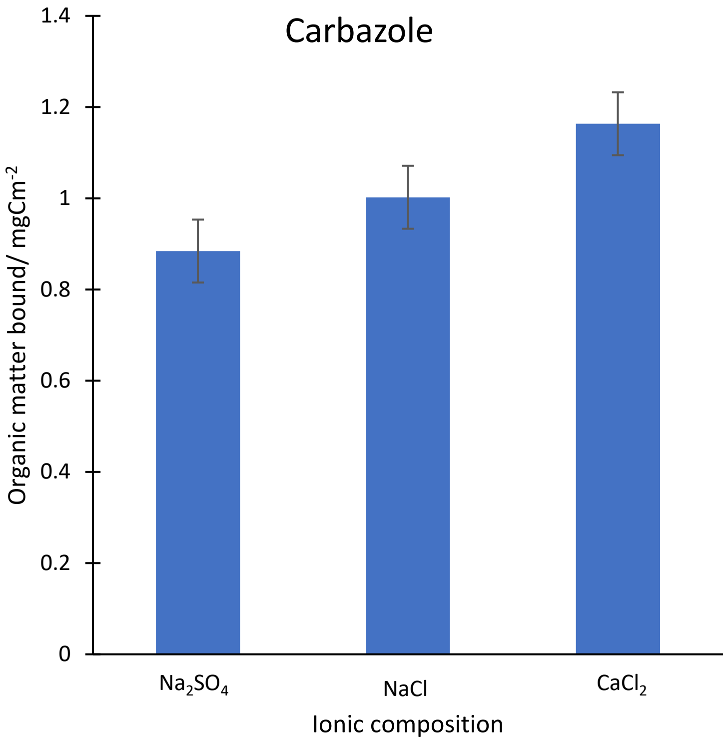


Figure 4.2. Sorption of carbazole to kaolinite in solutions of different ionic compositions.

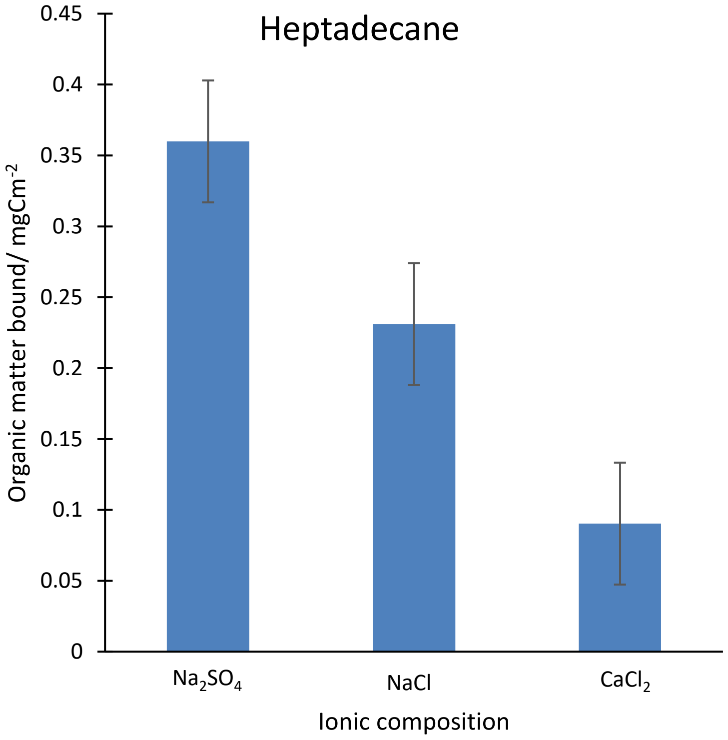


Figure 4.3. Sorption of heptadecane to kaolinite in solutions of different ionic compositions.

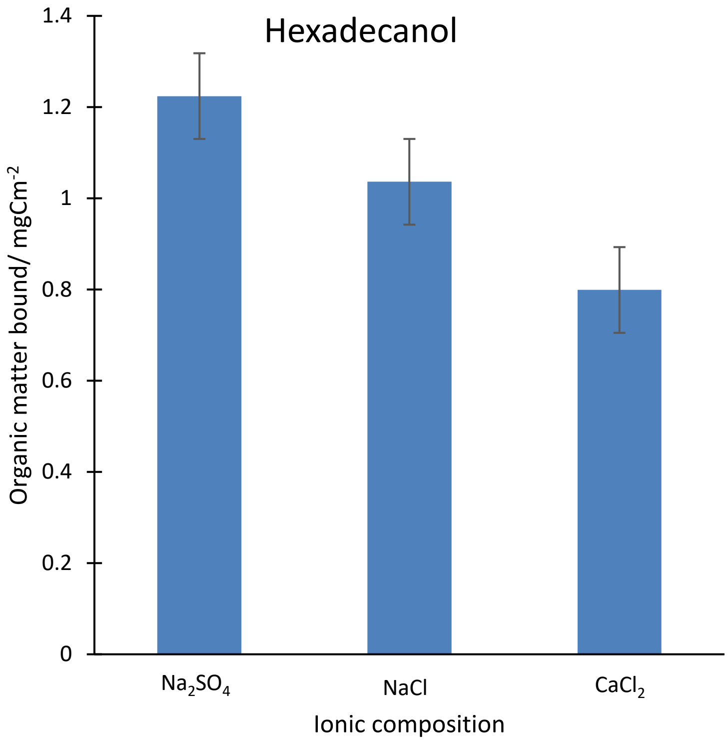


Figure 4.4. Sorption of hexadecanol to kaolinite in solutions of different ionic compositions.

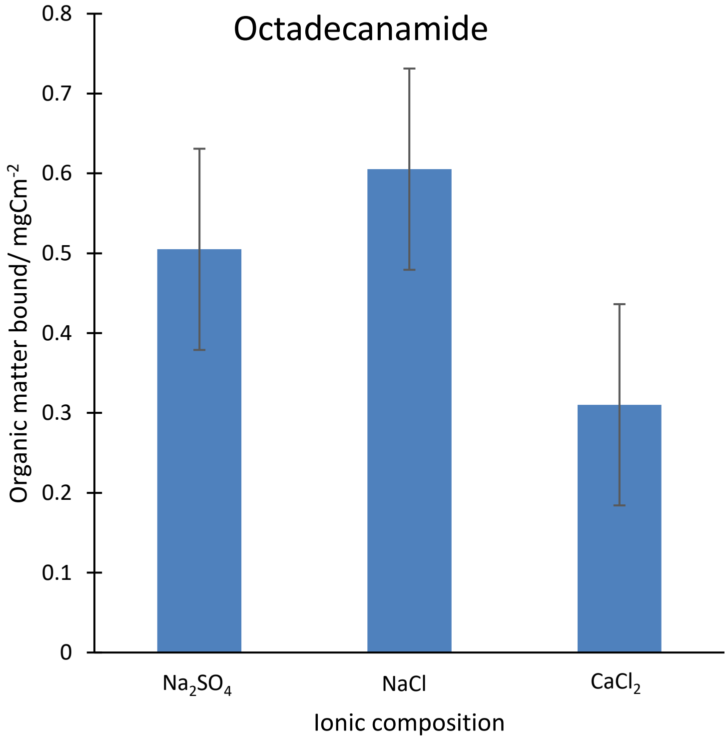


Figure 4.5. Sorption of octadecanamide to kaolinite in solutions of different ionic compositions.

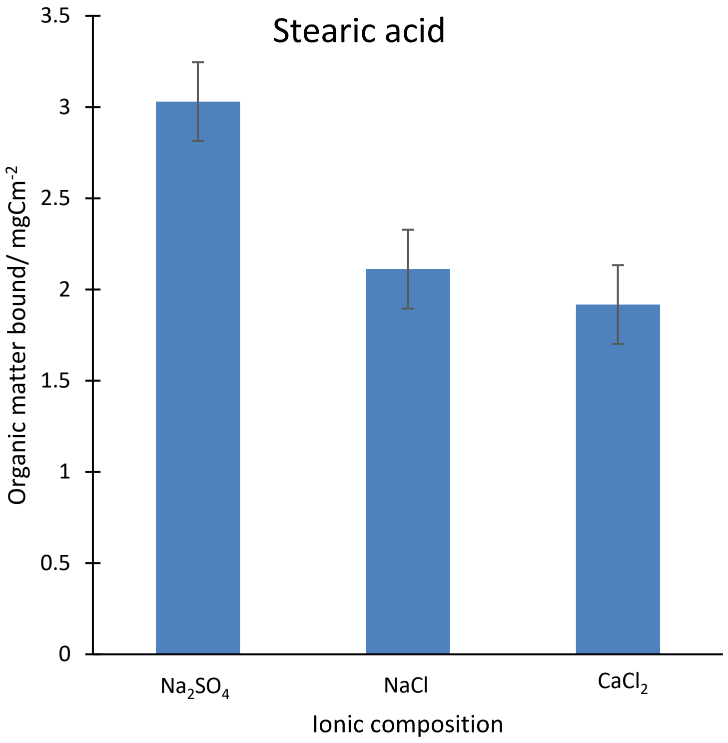


Figure 4.6. Sorption of stearic acid to kaolinite in solutions of different ionic compositions.

4.3.2 Ionic strength

Ionic strength experiments give an indication of the importance of Van der Waals interactions and anion and cation exchange. As the ionic strength is reduced the double layer around the mineral will increase, making it harder for the organic matter to approach the mineral and reducing Van der Waals interactions. However, anion and cation exchange are promoted by decreased ionic strength as this will reduce the number of competing ions. This means that increased bounding with increased ionic strength suggests Van der Waals interactions, whereas increased bonding with reduced ionic strength suggest anion or cation exchange.

In anthracene as the ionic strength is increased anthracene shows greater sorption to kaolinite (*Figure 4.7*) this increased sorption at higher ionic strength suggests that Van de Waals interactions are important, but that anion and cation exchange are not.

In carbazole sorption appears to decrease for the first three ionic strengths but then decreases for the highest ionic strength (*Figure 4.8*) which is not consistent with either mechanism. It could be that cation and anion exchange are important at the lower ionic strengths with Van der Waals interactions becoming more dominant at the higher ionic strengths. However, Van der Waals interactions should be weaker than anion and cation exchange meaning the highest ionic strength would not be expected to show the most sorption. In addition, carbazole is not a charged molecule meaning anion and cation exchange are unlikely. Given this it is likely that the shape of the graph is the result of experimental error.

In heptadecane highest sorption is shown at the lowest ionic strength with the next lowest ionic strength showing much lower sorption but then increasing with increased ionic strength at higher ionic strengths (*Figure 4.9*). The general trend for increased sorption at higher ionic strength implies Van der Waals interactions may be important. However, the difference between the sorption at different strengths is minimal and within experimental error.

Hexadecanol generally shows a trend of increased sorption at lower ionic strength, although the lowest ionic strength plots slightly below the previous point, but within experimental error (*Figure 4.10*). This suggest that anion exchange may be an important mechanism, with the lone pair on the oxygen enabling electron density donation onto the mineral surface.

Octadecanamide ionic strength data shows a curve shape with poor sorption seen at both high and low ionic strength (*Figure 4.11*). This is likely because ionic strength has a minimal effect on the strength of interaction. Suggesting, that neither anion/cation exchange nor Van der Waals interactions are important bonding mechanism in octadecanamide.

Stearic acid shows a strong trend of decreasing sorption at higher ionic strength (*Figure 4.12*). This suggests that anion exchange is important whereas Van der Waals interactions are not. With a pK_a of 4.75, stearic acid will be deprotonated and therefore negatively charged at pH 9 of artificial sea water, allowing interaction by anion exchange.

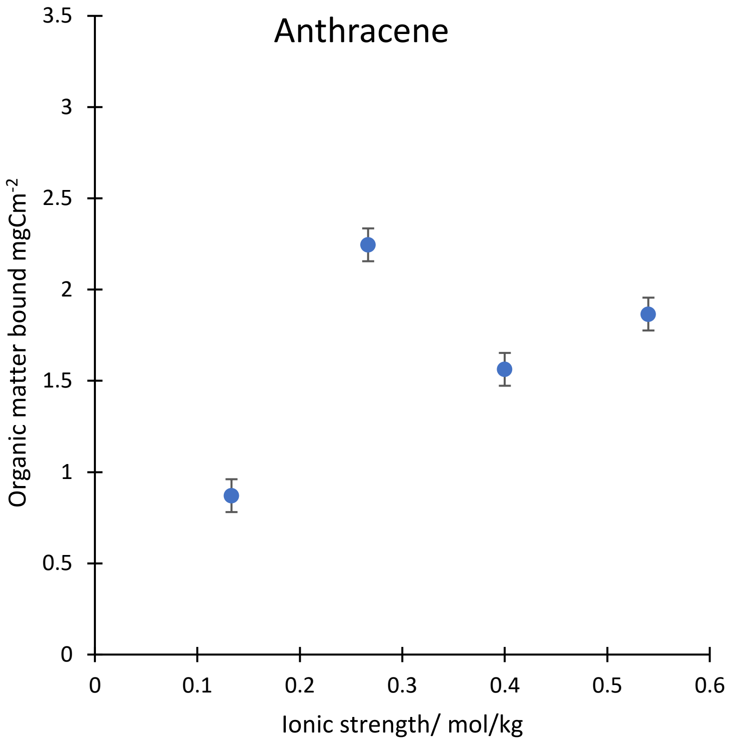


Figure 4.7. Sorption of anthracene to kaolinite at different ionic strengths.

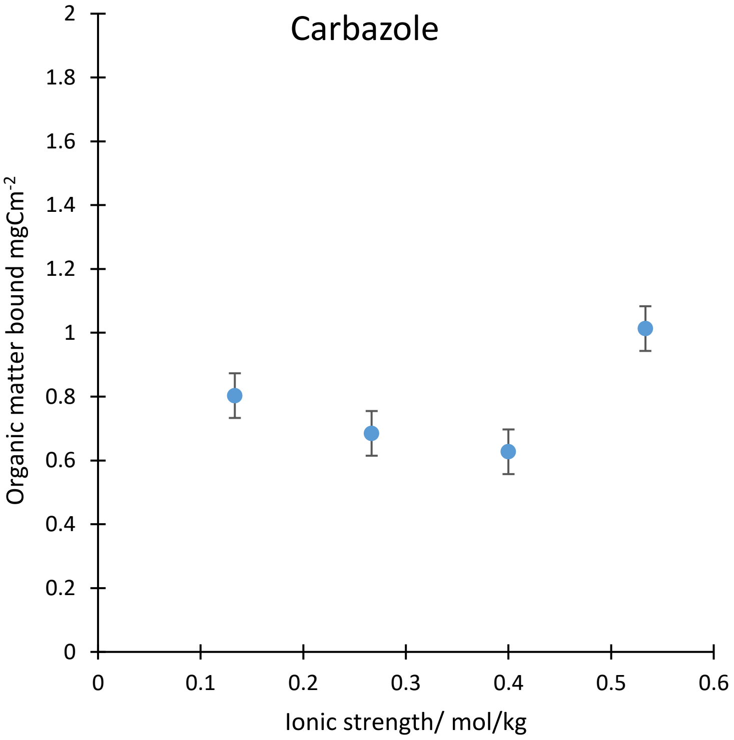


Figure 4.8. Sorption of carbazole to kaolinite at different ionic strengths.

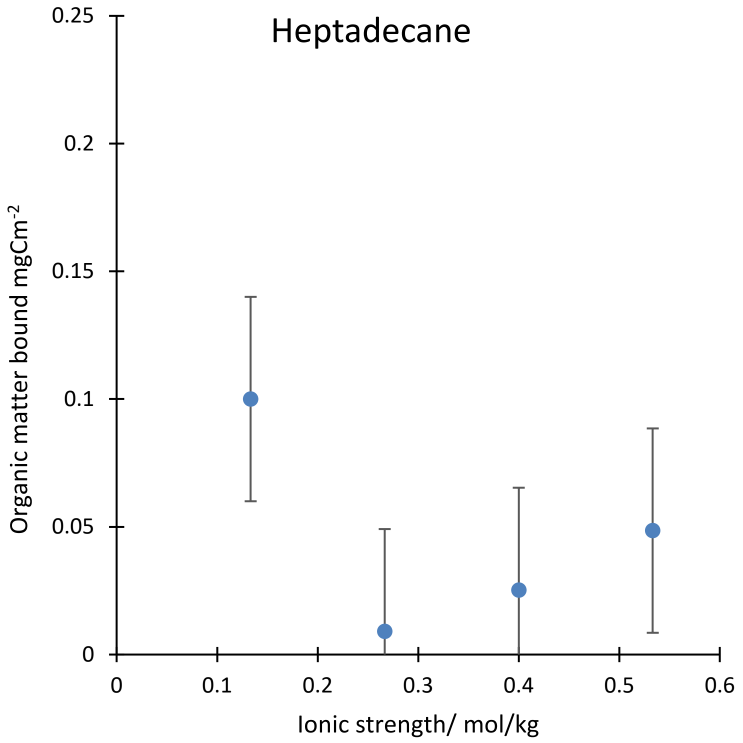


Figure 4.9. Sorption of heptadecane to kaolinite at different ionic strengths.

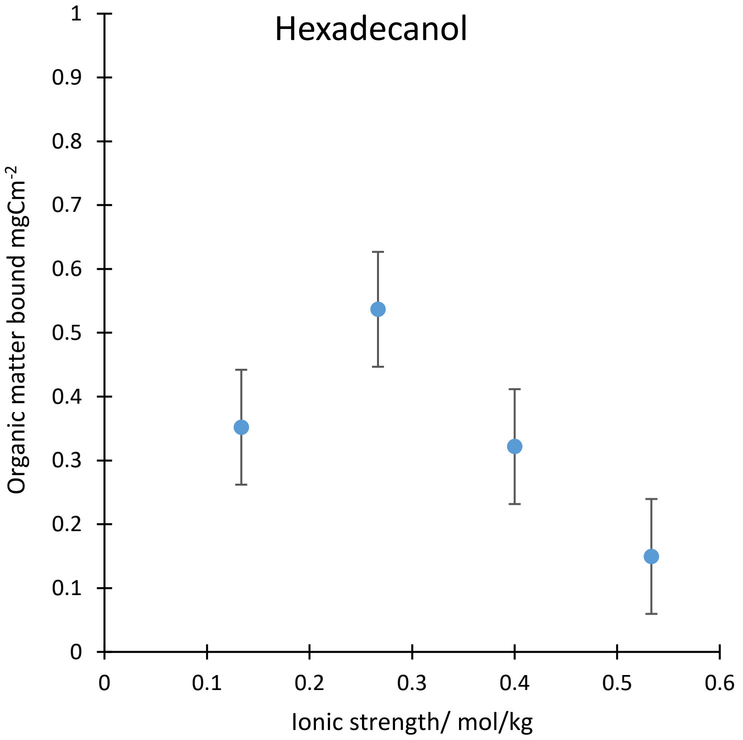


Figure 4.10. Sorption of hexadecanol to kaolinite at different ionic strengths.

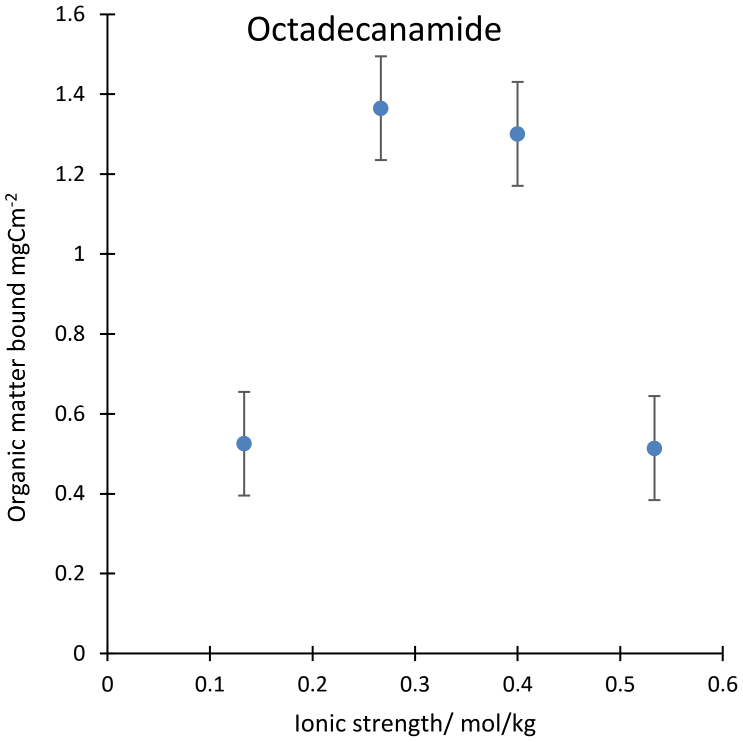


Figure 4.11. Sorption of octadecanamide to kaolinite at different ionic strengths.

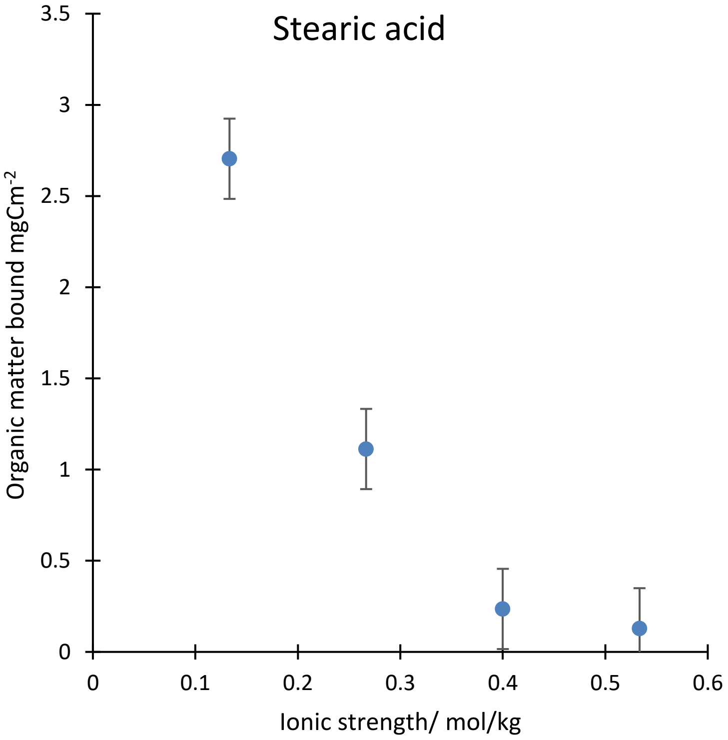


Figure 4.12. Sorption of stearic acid to kaolinite at different ionic strengths.

4.3.3 pH

The pH experiments allow investigation of hydrophobic interactions. Hydrophobic interactions are promoted in acid molecules at lower pH values because they become protonated and less charged. However, the picture is complicated by the minerals' pH dependent charge. The point of zero charge of kaolinite is approximately pH 3 (Tschapek et al., 1974). This means that above this point the mineral surface will become increasingly negatively charged, whereas below this point it will become increasingly positively charged.

Anthracene sorption at different pH values is very similar but with a slight increase at lower pH values (*Figure 4.13*). Anthracene has no acidic hydrogens, suggesting that this slight increase is due to the negative surface charge of kaolinite being reduced at lower pH values (Tschapek et al., 1974).

Carbazole shows reduced sorption at the higher pH values (*Figure 4.14*). This is likely to be due to protonation of the mineral at lower pH values as in anthracene.

In heptadecane sorption is again reduced at higher pH values as in the aromatic compounds this is likely to be due to protonation of the mineral at lower pH values (*Figure 4.15*).

Hexadecanol shows greater sorption at lower pH values (*Figure 4.16*). Although hexadecanol is capable of both protonation and deprotonation this is again likely to be due to protonation of the mineral surface. The point of zero charge in kaolinite is approximately pH 3 (Tschapek et al., 1974), the pK_a and pK_b of hexadecanol are 16.70 and -1.99, respectively. Therefore, in this pH range the compound will remain neutral. The increased sorption at lower pH is likely due to a more neutral surface being easier to approach for the high electron density OH group of hexadecanol.

Octadecanamide also shows better sorption at lower pH values (*Figure 4.17*). As in hexadecanol although octadecanamide is a weak base, it is likely this is due to reduction of the surface charge on the kaolinite. Octadecanamide has a pK_b of around – 0.5, so it is unlikely to be protonated, however the reduction in the mineral surfaces negative charge will make bonding more favourable.

As with previous compounds stearic acid shows increased sorption at lower pH values (*Figure 4.18*). However, with a pK_a of 4.75, stearic acid deprotonated will occur within this pH range. At pH 9 of artificial sea water it will be negatively charged but at pH 3, stearic acid begins to be protonated. Therefore, the slightly increased binding at lower pH is likely to be due to protonation of the mineral allowing the negatively charged stearic acid to approach more easily.

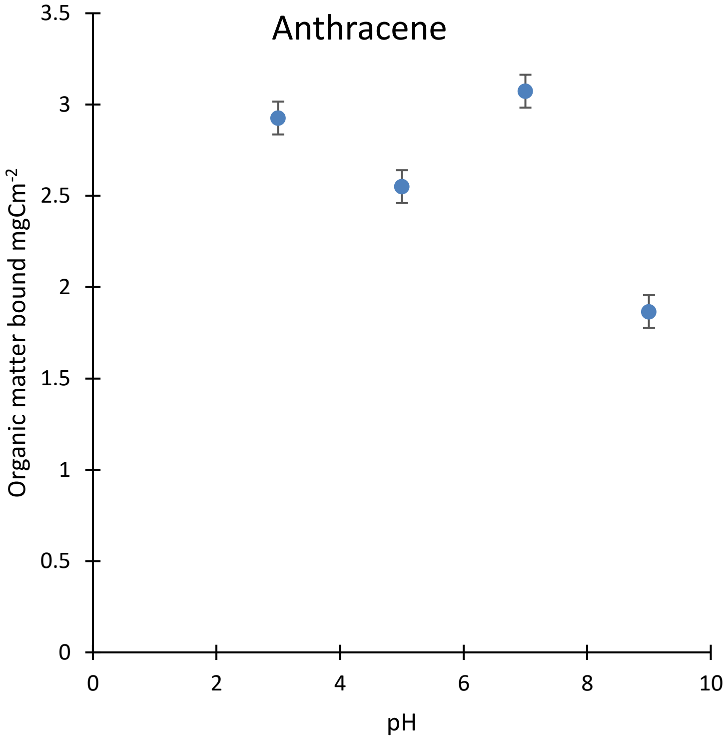


Figure 4.13. Sorption of anthracene to kaolinite at different pH.

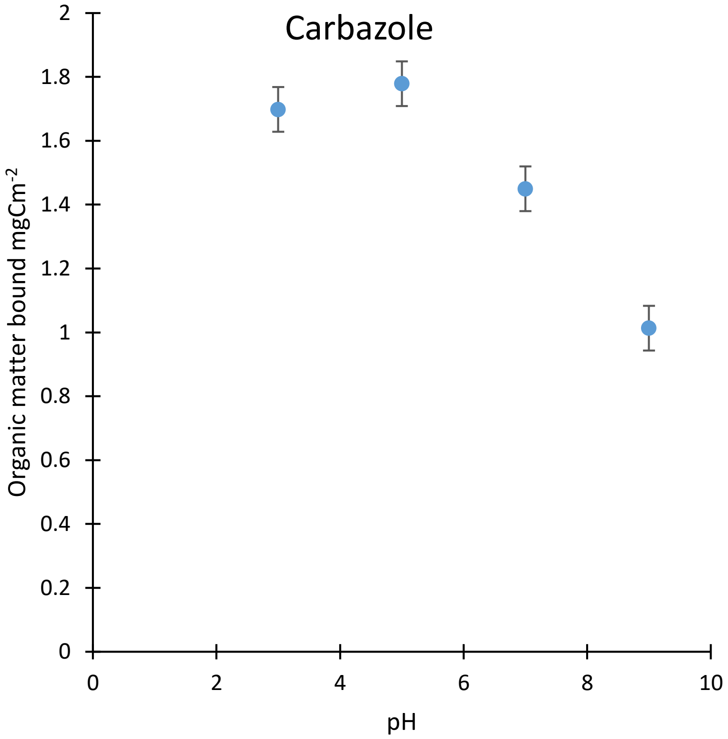


Figure 4.14. Sorption of carbazole to kaolinite at different pH.

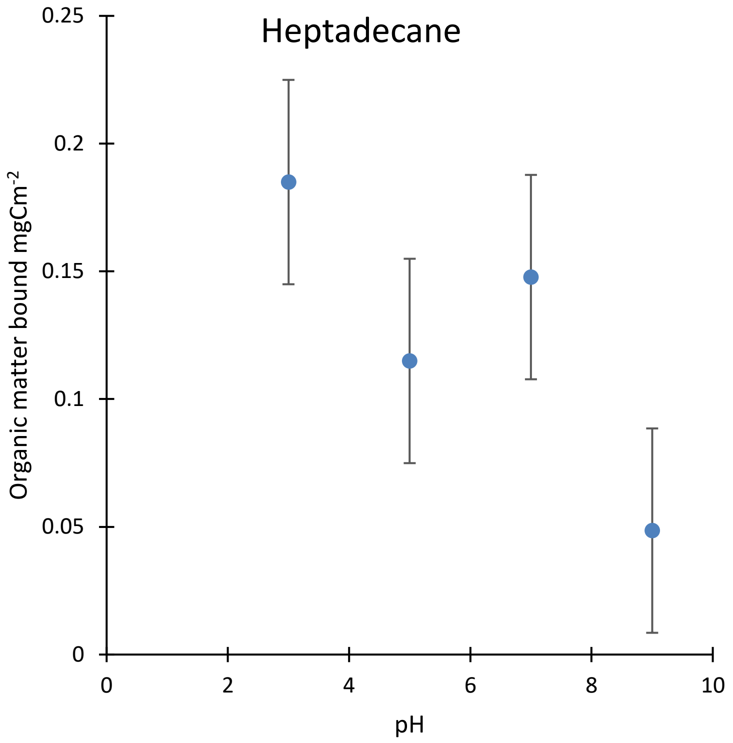


Figure 4.15. Sorption of heptadecane to kaolinite at different pH.

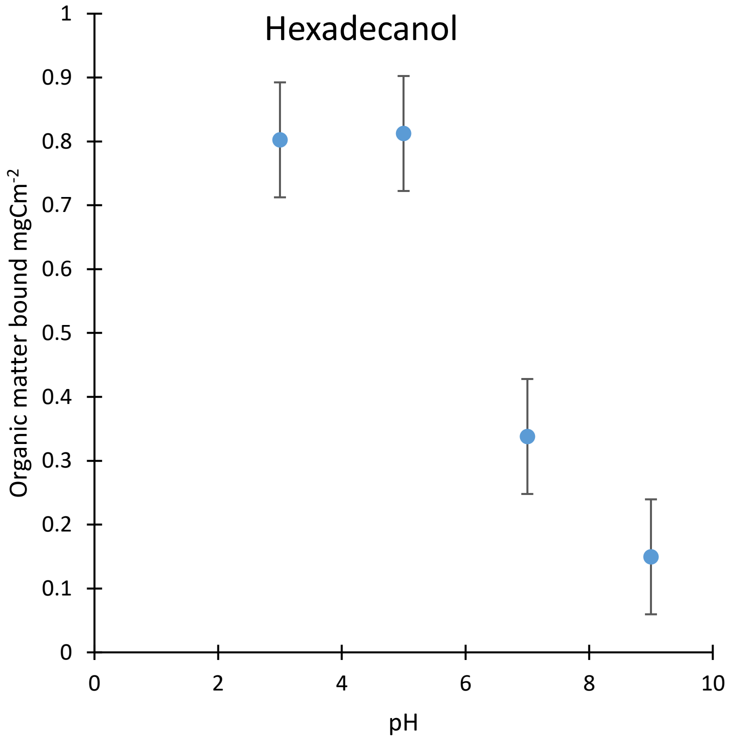


Figure 4.16. Sorption of hexadecanol to kaolinite at different pH

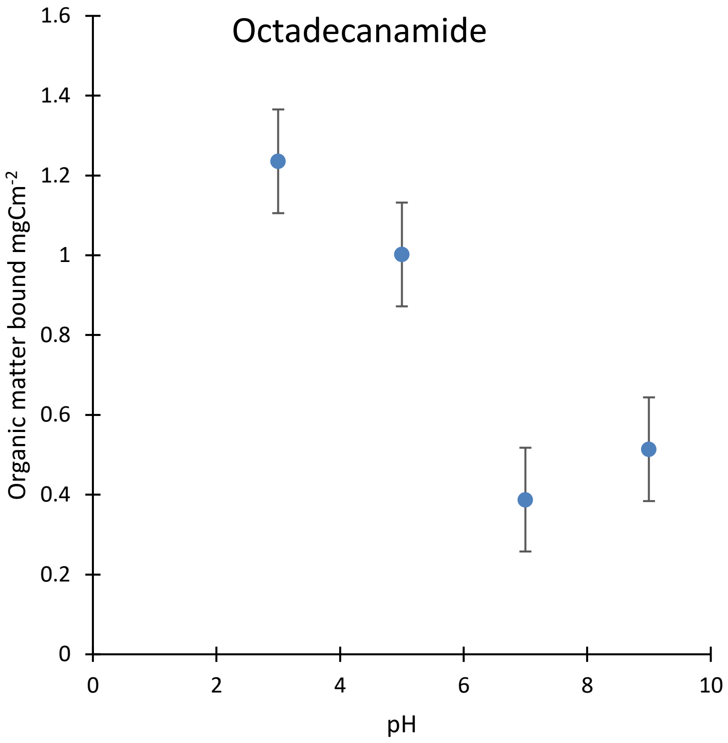


Figure 4.17. Sorption of octadecanamide to kaolinite at different pH.

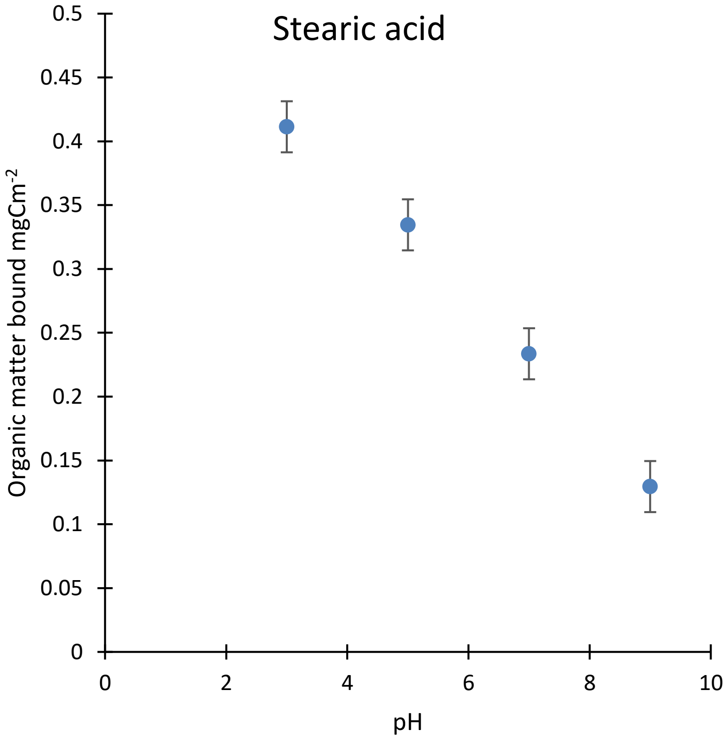


Figure 4.18. Sorption of stearic acid to kaolinite at different pH.

4.3.4 Temperature

Repeating the sorption isotherms at a second temperature allows an estimation of enthalpy of bonding.

In anthracene both temperatures show a linear response with sorbed organic matter increasing with increased dissolved organic matter (*Figure 4.19*). The steeper gradient is seen at 20°C rather than 11°C, showing that the enthalpy of sorption will be positive. Calculation using the Arrhenius equation gives a value of 30.1KJmol^{-1}.

In carbazole as in anthracene a linear response is shown at both temperatures, however the gradient is steeper at the lower temperature of 11°C (*Figure 4.20*). This gives a negative enthalpy which can be calculated as -59.7 KJmol^{-1}.

In heptadecane the response at 20°C shows a high degree of spread from the line of best fit questioning whether this is a truly linear response (*Figure 4.21*). Whereas the 11 °C data does fit well. The higher gradient at the higher temperature means that the enthalpy is positive at 128.7 KJmol^{-1}.

Hexadecanol shows a poor correlation in the 11°C isotherm but all points are higher than corresponding points at 20°C (*Figure 4.22*). This means that the enthalpy will be negative. It was calculated at -96.5 KJmol^{-1}; however, the poor correlation means this number will have a high degree of error associated.

In octadecanamide the data for both temperatures are very similar and well within experimental error, suggesting that to obtain a reliable value for the enthalpy of bonding a wider temperature range is needed (*Figure 4.23*). However, 20°C shows a slightly higher gradient, and the enthalpy can be calculated as 1.47 KJmol^{-1}.

In stearic acid both temperatures show good correlation with increased sorption with increased dissolved matter (*Figure 4.24*). Values at the 2 temperatures are similar but less so than in octadecanamide and not within experimental error at the higher values. A steeper gradient is show by the 20°C data giving a positive enthalpy determined to be 40KJmol^{-1}.

Overall, these calculations would be improved if they were repeated over a wider temperature range with a larger number of isotherms at different temperatures. However, these results should give an indication of the sign and magnitude of the enthalpy of bonding.

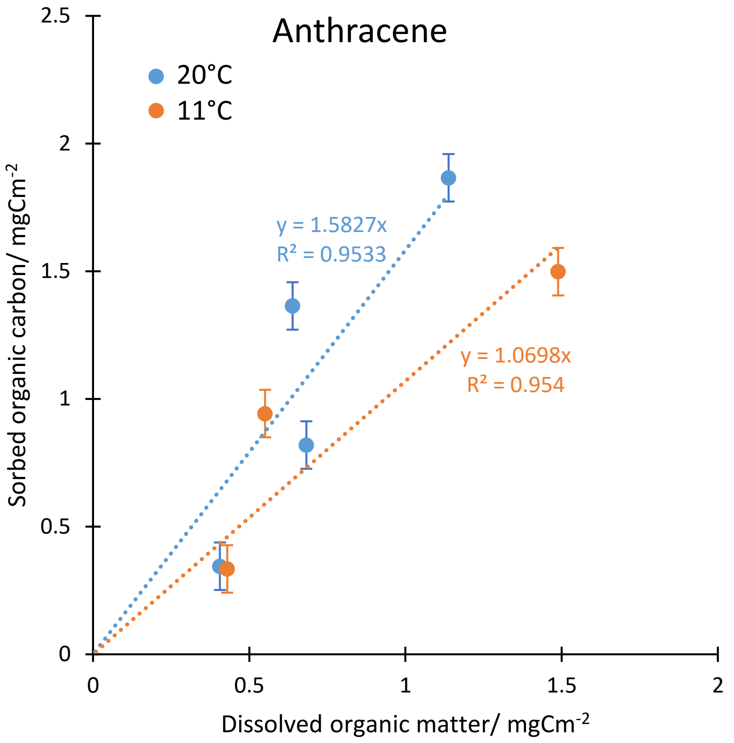


Figure 4.19 Anthracene isotherm at 11°C and 20°C.

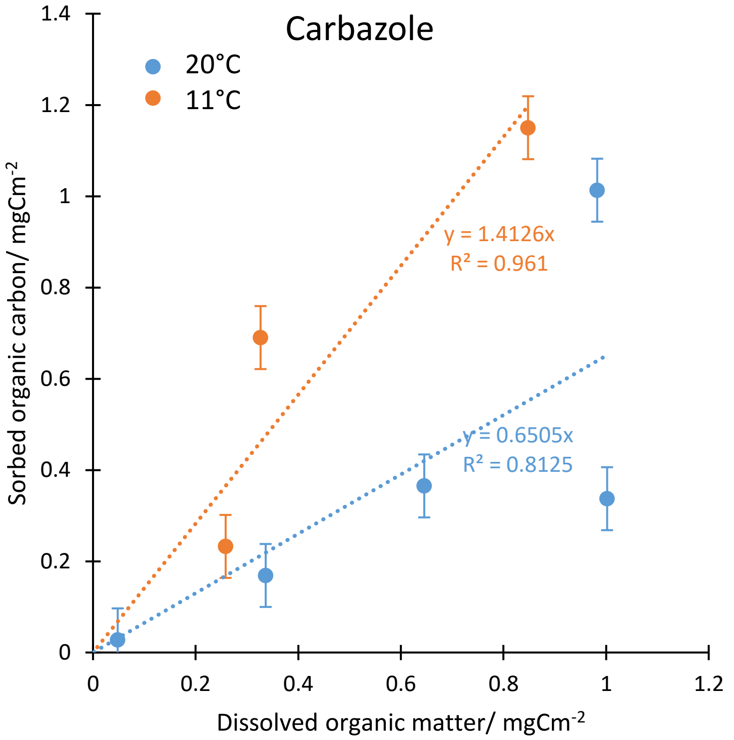


Figure 4.20 Carbazole isotherm at 11°C and 20°C.

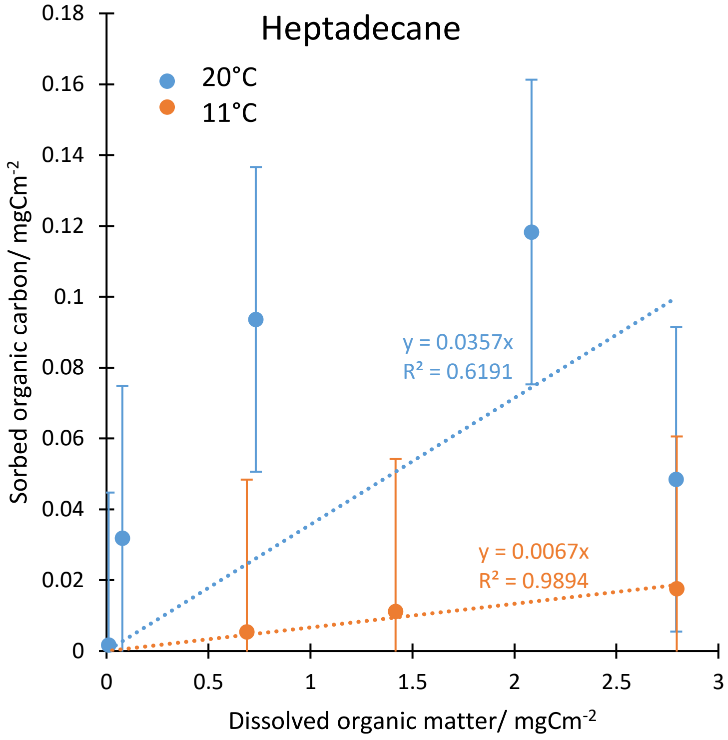


Figure 4.21 Heptadecane isotherm at 11°C and 20°C.

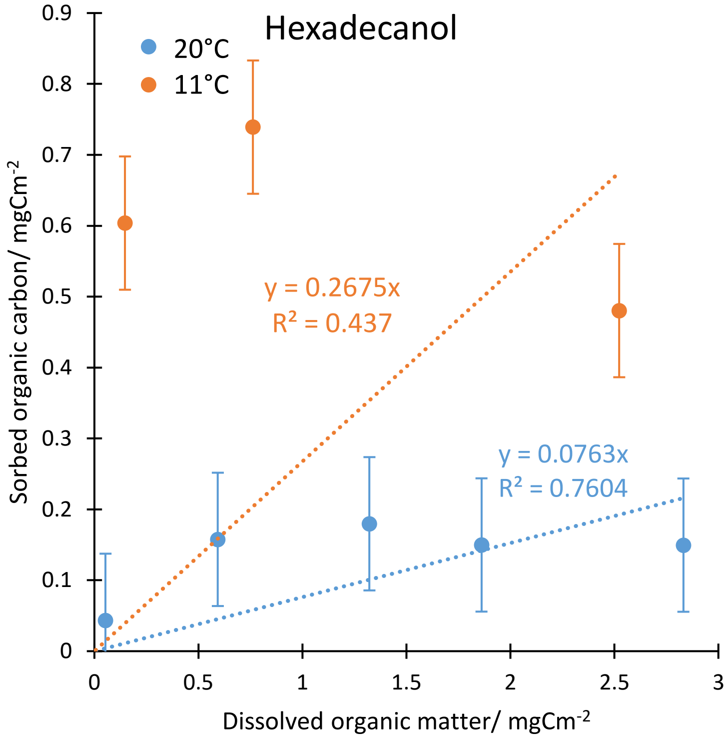


Figure 4.22 Hexadecanol isotherm at 11°C and 20°C.

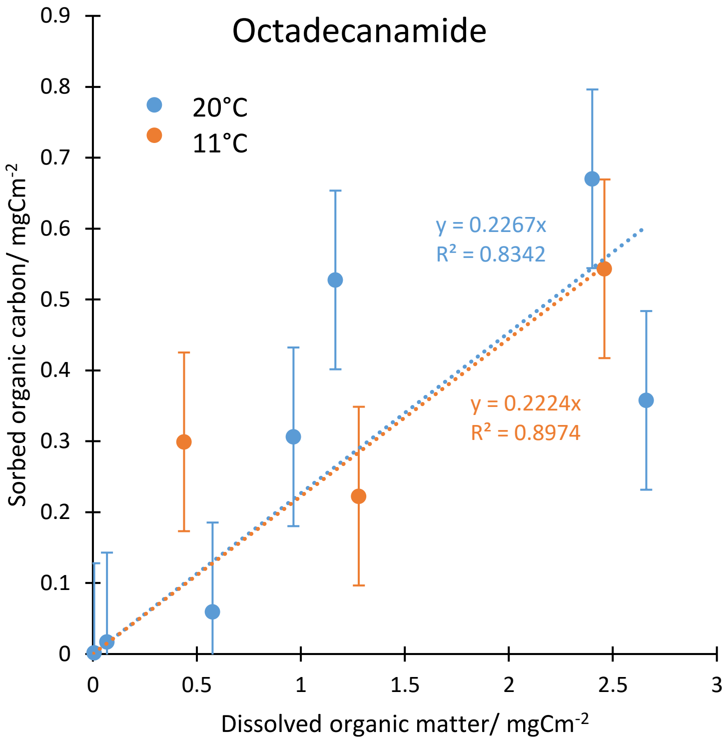


Figure 4.23 Octadecanamide isotherm at 11°C and 20°C.

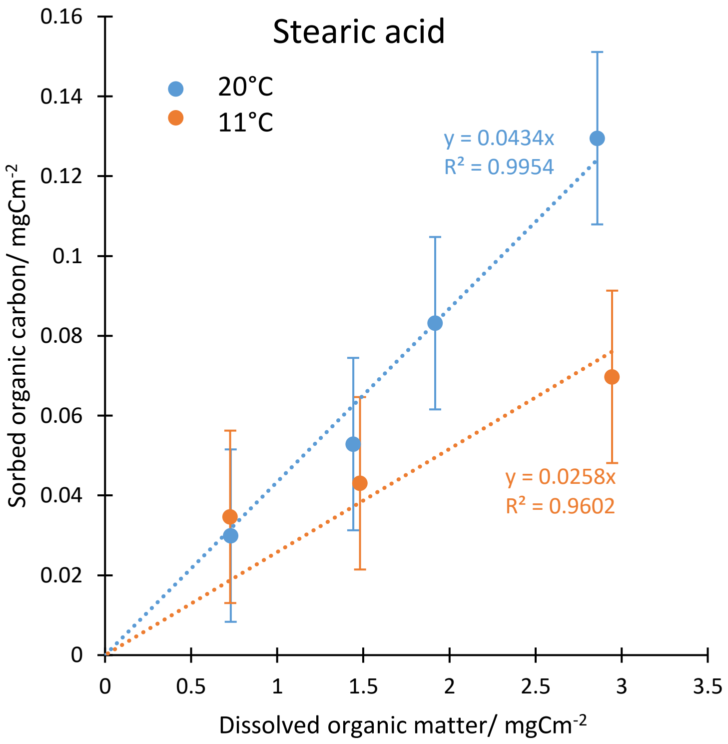


Figure 4.24 Stearic acid isotherm at 11°C and 20°C.

4.3.5 Implications for mechanism

Combining the different conditions allows an estimation of the mechanisms involved in the binding of the different compounds to kaolinite.

In anthracene the ionic composition data suggests that neither ligand exchange nor cation bridging are important mechanisms for anthracene. Increased sorption at higher ionic strength suggests that Van de Waals interactions are important, but that anion and cation exchange are not. This is to be expected as anthracene is an uncharged molecule. Anthracene also has no acidic hydrogens, suggesting that the slightly increased sorption at lower pH is likely due to the negative surface charge of kaolinite being reduced at lower pH values (Tschapek et al., 1974). The enthalpy of interaction is positive, suggesting this is an entropy driven reaction, implying that the main operating mechanism is hydrophobic interactions, rather than Van der Waals interactions which are enthalpy favourable. However, the enthalpy data was only calculated with two similar temperatures which is likely to have reduced its accuracy. Also, the increased sorption of aromatic compounds shown in Chapter 3 suggest that Van der Waal interactions are likely to be important because the delocalised electrons in aromatic compounds allow them to form stronger Van der Waals interactions. Thus, hydrophobic and Van der Waals interactions are both likely to be important in anthracene.

Ionic composition data in carbazole suggest a small amount of ligand exchange and cation bridging. However, as carbazole is also uncharged, cation bridging is an unlikely mechanism. Aromatic compounds are able to act as ligands using their aromatic electrons to donate electron density to metal ions. This would also explain the negative enthalpy of bonding. The ionic strength data does not show a clear picture, possibly the result of experimental error. As in anthracene the effect of pH is probably due to the protonation of the mineral reducing the surface charge at lower pH values as the nitrogen lone pair on carbazole is delocalised into the aromatic ring and therefore not available for protonation. Overall, the results suggest that interactions in carbazole are Van der Waals interactions possibly together with some ligand exchange and hydrophobic interactions.

Heptadecane ionic composition data indicate that neither cation bridging, nor ligand exchange are important in heptadecane binding to kaolinite. Ionic strength data imply Van der Waals interactions are important, with greater bonding at higher ionic strengths. As in the aromatic compounds the increased binding at lower pH is likely to be due to reduced surface charges on the kaolinite as there are no protonatable sites on heptadecane. The enthalpy of binding is positive, i.e. highly unfavourable, due to the limited data used to calculate this, there is likely to be a large error. However, it may be explained by a high contribution from entropy driven hydrophobic interactions. Overall, this suggests that hydrophobic and Van der Waal interactions are important in the binding of heptadecane to kaolinite.

In hexadecanol neither ligand exchange nor cation bridging appear to be of importance according to the ionic composition data. Increased sorption at lower ionic strength suggest that anion exchange might be an important mechanism. Although hexadecanol does not have a negative charge, it has lone pairs that enable electron density donation onto the mineral surface. The effect of pH, greater sorption at lower pH, is again likely to be due to protonation of the mineral surface. A more neutral surface being easier to approach for the high electron density OH group of hexadecanol. The highly negative enthalpy of interaction is indicative of a strong interaction, consistent with anion exchange. Although the enthalpy data is less reliable, together with the ionic strength data, it suggests that anion exchange is a key mechanism for hexadecanol binding to kaolinite.

Some ligand exchange may be present in octadecanamide although the reduction in sorption seen in Na_2SO_4 is limited and within experimental error. In addition, the delocalisation of nitrogen lone pair into the carbonyl group means it is less available for use as a ligand. The enthalpy of bonding is also much lower than would be expected were ligand exchange to be an important mechanism. The composition data show that cation bridging is not important. Ionic strength data suggests that neither anion/cation exchange nor Van der Waals interactions are important, as there is poorer bonding at both high and low ionic strength. This is likely because ionic strength has a minimal effect on the strength of interaction. Although octadecanamide is a weak base, it has a pK_b of around – 0.5, so it is unlikely to be protonated. Therefore, the increased sorption at lower pH is likely to be due to the reduction of the surface charge on the kaolinite. Overall, this suggests that bonding in octadecanamide is predominately due to hydrophobic interactions, which is consistent with the poor solubility of octadecanamide in both water and isopropyl alcohol.

Stearic acid composition data show neither ligand exchange nor cation bridging appear to be of importance. The decreased sorption at higher ionic strength suggests that Van der Waals interactions are not important, but anion exchange may be. With a pK_a of 4.75, stearic acid is deprotonated and therefore negatively charged at pH 9 of artificial seawater. At pH 3, stearic acid begins to be protonated, therefore the slightly increased binding at lower pH is likely to be due to protonation of the mineral allowing the negatively charged stearic acid to approach more easily. The enthalpy of bonding is highly positive suggesting an entropy driven reaction so that hydrophobic interactions may also be important. This suggests that both anion exchange and hydrophobic interactions may be important.

4.3.6 Comparison with previous work

A summary of the mechanism found in this study can be found in *Table 4.1* and compare to mechanism found in previous studies shown in *Table 4.2*.

Table 4.1. Comparison of important mechanisms for the different compounds used in this study + represents mechanism present, - represents those that are absent

Organic matter	**Mineral**	**Van der Waals**	**Cation bridging**	**Anion exchange**	**Cation exchange**	**Ligand exchange**	**Hydrophobic interactions**
Anthracene	Kaolinite	+	-	-	-	-	+
Carbazole	Kaolinite	+	-	-	-	+	+
Heptadecane	Kaolinite	+	-	-	-	-	+
Hexadecanol	Kaolinite	-	-	+	-	-	-
Octadecanamide	Kaolinite	-	-	-	-	-	+
Stearic acid	Kaolinite	-	-	+	-	-	+

Table 4.2 *Comparison of important mechanisms which are important in different organic matter-mineral interactions. + represents mechanism present, - represents those that are absent. V. d. W.= Van der Waals interactions, C.B.= Cation bridging, A.E.=anion exchange, C.E. Cation exchange, L.E.=ligand exchange and H.I.= Hydrophobic interactions.*

Organic matter	**Mineral**	**Reference**	**V. d. W.**	**C.B.**	**A.E.**	**C. E.**	**L. E.**	**H. I.**
Pore-water organic matte r	Montmorillonite	(Arnarson and Keil, 2000)	+	+	-	-	+	-
Humic acids	Montmorillonite	(Feng et al., 2005)	+	+	-	-	-	+
Soil organic matter	Goethite	(Mikutta et al., 2007)	+	-	-	-	+	-
Soil organic matter	Pyrophyllite	(Mikutta et al., 2007)	+	-	-	-	+	-
Soil organic matter	Vermiculite	(Mikutta et al., 2007)	-	+	-	-	+	-

The mechanisms found in this work are notably different from those of previous studies. There are a number of likely reasons for this. Firstly, previous studies concentrated on dissolved and therefore soluble organic matter. Thus, the absence of hydrophobic interactions in this organic matter is to be expected as these are only important where dissolution of the organic matter is unfavourable. The majority of the compounds used in this study were poorly soluble. Both dissolved and particulate organic matter need to be considered, as both are important within the natural environment (Lee et al., 2009). Secondly, the limited importance of ligand exchange is likely to be due to the low functionality of compounds used in this study. Due to the chelate effect, ligands are much more effective when they have multiple functional groups and are able to form multiple bonds from the same compound. This is more likely to occur with the large compounds present in natural organic matter. Finally, all of the compounds used in this study, aside from stearic acid, are uncharged under the conditions used. Natural organic matter may be more likely to be charged (i.e., able to interact by cation bridging). Van der Waals interactions have been shown to be important in most cases which is likely to be due to their universal nature, i.e. all compounds are capable of forming Van der Waals interactions.

4.4 Conclusions

This study used changing conditions of pH, ionic strength, ionic composition and temperature to determine the mechanisms at work in the binding of six compounds (anthracene, carbazole, heptadecane, hexadecanol, octadecanamide and stearic acid) to the clay mineral kaolinite. The mechanisms observed (hydrophobic interactions, Van der Waals forces, anion exchange and ligand exchange) are consistent with those that would be expected for the chemical structure of these compounds. However, a number of differences from previous studies were noted. Most notably: a greater of presence hydrophobic interaction, a lower presence of ligand exchange and an absence of cation bridging. These differences are to be likely the result of the different organic matter sources used. Although this study provides new insights into the interactions between mineral surfaces and OM, further work with larger, more complex organic matter is needed to determine if the greater preference for ligand exchange reported in previous studies is valid. Furthermore, due to the exclusion of particulate organic matter in previous studies, the results obtained may not have reflected the full range of effects that would be exhibited by natural organic matter. Therefore, further non-specific studies into the mechanisms of binding of natural organic matter should be undertaken, as it is likely that both mechanisms found here and in previous studies will be of importance. It would also be beneficial to conduct experiments with a broader range of temperatures in order to provide a more accurate prediction of the enthalpy of bonding.

Chapter 5 Importance of mineral type on the extent of organic matter-mineral sorption

5.1 Introduction

Clay and iron minerals have both been shown to be important in organic matter-mineral interactions in marine sediments (Lalonde et al., 2012, Mayer, 2004). Clays provide a high surface area for organic matter to interact with (Ransom et al., 1998), and iron minerals are able to complex strongly with the organic matter (Barber et al., 2014). The organic matter-mineral ratio determines whether the surface area or the strength of interaction is more important for organic matter; The strength of the interaction is more important where the organic matter-mineral ratio is low, and the surface area available is more important where the ratio is high (Saidy et al., 2013, Saidy et al., 2015). This is likely because at low organic matter concentrations weakly bound organic matter is able to desorb and be degraded. This means that the minerals which provide the greatest protection can vary depending on the organic matter concentration. However, the nature of the mineral is important to the preservation of organic matter, with strong correlations between clay content and organic matter preservation (Kennedy and Wagner, 2011) and up to 20% of organic matter in marine sediments observed to be associated with iron (Lalonde et al., 2012). Preference for one type of organic matter over another can also vary between mineral types, as can the interaction mechanism (Newcomb et al., 2017, Mikutta et al., 2007). Therefore, the presence of different minerals in different locations could lead to the preferential preservation of different types of organic matter. Studies of natural organic matter have typically found greater sorption to iron minerals than to clays (Mikutta et al., 2007, Shaker et al., 2012). However, it is unknown whether these differences are due to iron minerals having a preference for organic matter types that are more common in marine environments or if they have a great capacity for sorption of organic matter. By investigating interactions between three different minerals and six model compounds (anthracene, carbazole, heptadecane, hexadecanol, octadecanamide and stearic acid) this study aims to determine which of the above is more important. The minerals that will be investigated are kaolinite, representing 1:1 clays; bentonite representing 2:1 clays; and goethite representing crystalline iron hydroxides.

5.2 Material and methods

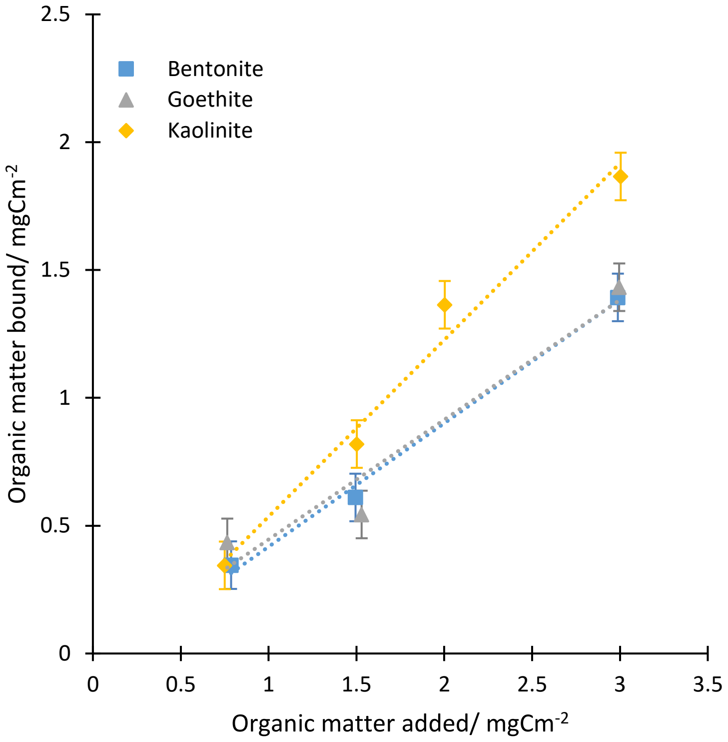
The methodology used in this investigation is detailed in Chapter 2. In brief, the compounds in *Table 2.1* were added, individually and in combination, to a suspension of kaolinite, bentonite, or goethite. For bentonite and goethite samples, the organic matter concentration was adjusted to produce the same organic matter: mineral ratio as in kaolinite with 0.5g of mineral. Sorption was monitored by isolating the mineral using centrifugation. The mineral was then extracted using solvent extraction and the extract analysed by GC-MS.

5.3 Results and discussion

Results are presented initially for individual compounds on different minerals and then for different minerals with all six compounds.

5.3.1 Anthracene

All three minerals show a linear response, with greater sorption achieved as more anthracene is added. Very similar responses are shown by bentonite and goethite, both achieving sorption of 1.4mgCm^{-2} at the highest concentration of added anthracene, 3.0mgCm^{-2}. Kaolinite sorption is similar but slightly greater achieving 1.9mgCm^{-2} for 3.0 mgCm^{-2} anthracene added.



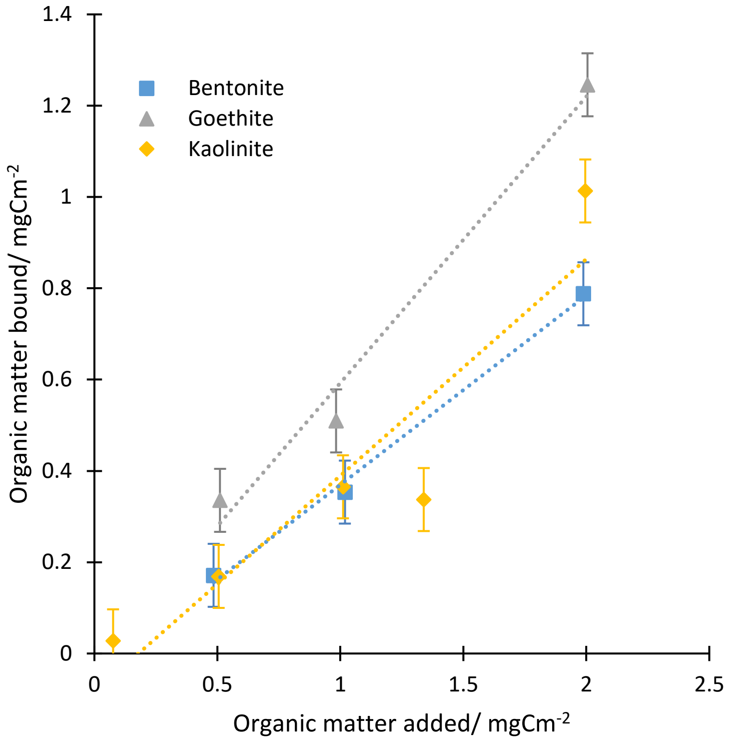
Mineral	Line of best fit	R^2 value
Bentonite ■	y = 0.4831x - 0.0655	$R^2 = 0.99$
Goethite ▲	y = 0.4685x - 0.0226	$R^2 = 0.94$
Kaolinite ◆	y = 0.6912x - 0.1559	$R^2 = 0.98$

Figure 5.1. Sorption of Anthracene to different minerals.

The similar sorption seen between the three minerals is likely because anthracene interactions are non-specific, Van der Waal and hydrophobic interactions. This will mean the difference in mineral surfaces are less likely to have an effect. The slight preference for kaolinite might be due to lower surface charge than bentonite (Satterberg et al., 2003) and fewer active hydroxyl groups than goethite (Meier et al., 1999), which may make its surface more preferable for hydrophobic interactions.

5.3.2 Carbazole

Carbazole also shows a positive linear response in all three minerals. Greatest sorption is seen in goethite followed by Kaolinite and bentonite. The highest sorption was achieved at the highest concentration of added carbazole, 2.0 mgCm^{-2}; this was 1.2, 1.0 and 0.8 mgCm^{-2} for goethite, kaolinite, and bentonite, respectively.



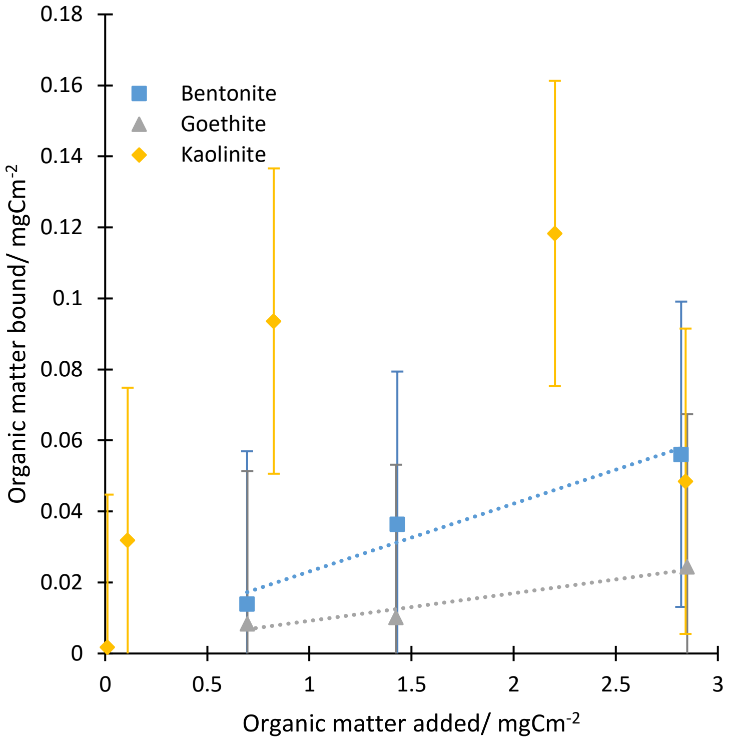
Mineral	Line of best fit	R^2 value
Bentonite ■	y = 0.4148x - 0.0452	R^2 = 0.99
Goethite ▲	y = 0.6272x - 0.0345	R^2 = 0.98
Kaolinite ◆	y = 0.4745x - 0.0851	R^2 = 0.87

Figure 5.2. Sorption of carbazole to different minerals.

Chapter 4 suggests that carbazole is interacting via a ligand exchange mechanism. The ligand exchange mechanism involves hydroxyl groups on the mineral surface. Goethite has a higher number of these hydroxyl groups than both kaolinite and bentonite (Meier et al., 1999, Song and Sandí, 2001). This higher number of potential sorption sites is the likely cause of the greater carbazole sorption to goethite.

5.3.3 Heptadecane

Heptadecane shows a linear response on bentonite and goethite but not on kaolinite. Kaolinite appears to plateau but with greater sorption, 0.1 mgCm^{-2}, shown at the penultimate concentration added, 2.2 mgCm^{-2}, than at the highest added concentration, 2.8 mgCm^{-2}, which shows a sorption of 0.05 mgCm^{-2}. Bentonite and goethite achieve lower levels of sorption 0.06 and 0.02 mgCm^{-2} respectively both at the added concentration of 2.8 mgCm^{-2}.



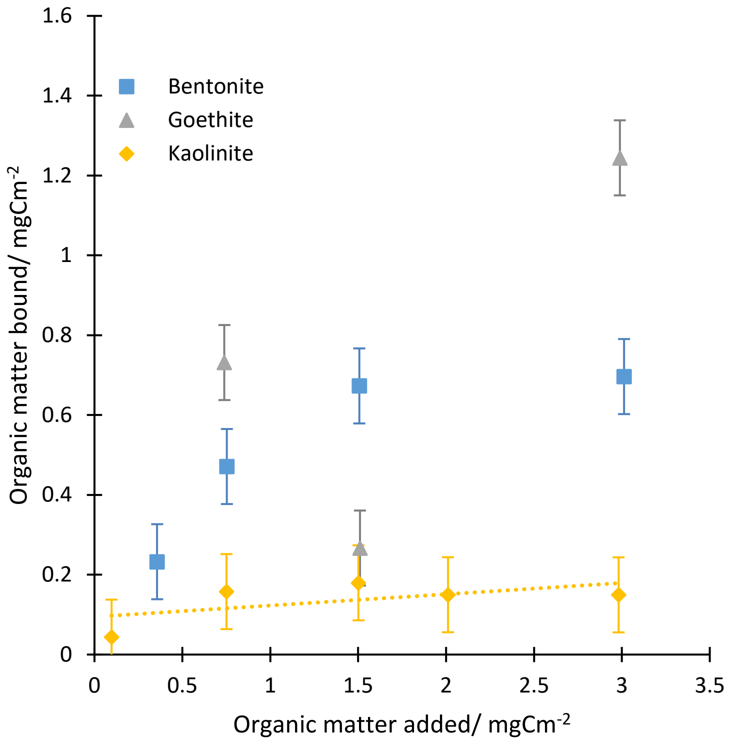
Mineral	Line of best fit	R^2 value
Bentonite ■	y = 0.0191x + 0.004	$R^2 = 0.96$
Goethite ▲	y = 0.0078x + 0.0014	$R^2 = 0.95$
Kaolinite ◆	Non-linear response	

Figure 5.3. Sorption of Heptadecane to different minerals.

Sorption for heptadecane is low for all three minerals. This is because it lacks functional groups to interact strongly with minerals. As a result, interactions are via Van der Waals and hydrophobic interactions. As in anthracene this preference for hydrophobic surfaces is the likely cause of the preference for kaolinite over bentonite and goethite, due to bentonite's higher surface charge (Satterberg et al., 2003) and goethite's increased hydroxyl groups (Meier et al., 1999).

5.3.4 Hexadecanol

In hexadecanol kaolinite shows the lowest response but seems to be the only mineral with a linear response. At the added hexadecanol concentration of 3.0 mgCm^{-2} sorption of only 0.15 mgCm^{-2} is achieved. The second highest sorption is shown by bentonite which appears to plateau to 0.7 mgCm^{-2} for added concentration of 1.5 and 3.0 mgCm^{-2}. The greatest sorption is shown by goethite which achieves 1.2 mgCm^{-2} at 3.0 mgCm^{-2}, however this shows neither a linear nor a plateau response. The lowest sorption is achieved at the middle point, likely the result of experiment error, although this is hard to clarify without more data points.



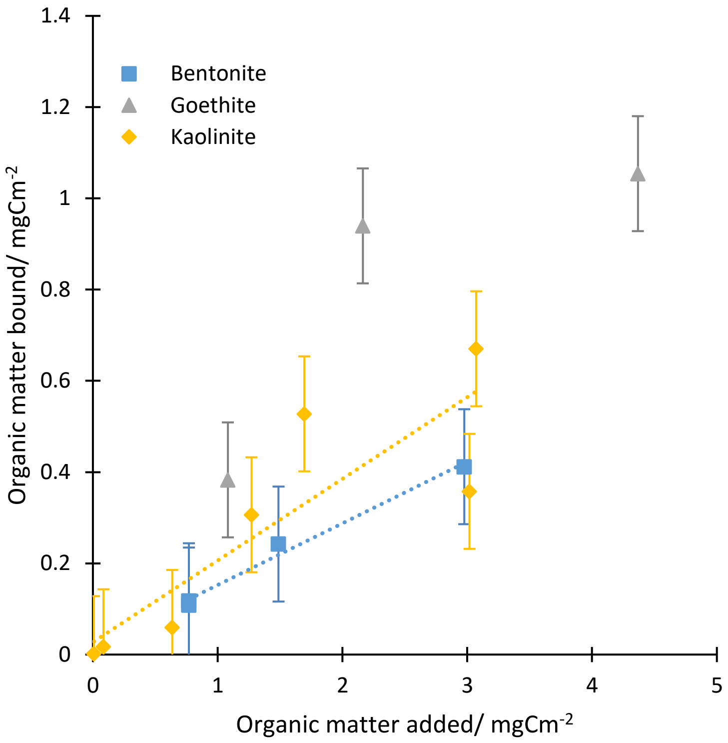
Mineral	Line of best fit	R^2 value
Bentonite ■	Non-linear response	
Goethite ▲	Non-linear response	
Kaolinite ◆	$y = 0.0283x + 0.0946$	$R^2 = 0.35$

Figure 5.4. Sorption of Hexadecanol to different minerals.

The order of mineral sorption, with goethite showing the greatest sorption followed by bentonite then kaolinite, is consistent with the anion exchange capacity of these minerals (goethite > bentonite > kaolinite) (Ioannou et al., 2013, Mclaughlin et al., 1981, Schell and Jordan, 1959). Chapter 4 showed that anion exchange is the main mechanism seen in the sorption of hexadecanol to kaolinite. The correlation between the mineral's anion exchange capacity and hexadecanol sorption suggests this mechanism is occurring in all three minerals.

5.3.5 Octadecanamide

The greatest sorption is achieved by goethite which appeared to be starting to plateau at 4.4 $mgCm^{-2}$ with an achieved sorption of 1.1 $mgCm^{-2}$. The next highest sorption is shown on kaolinite with a linear response reaching 0.67 $mgCm^{-2}$ sorbed for 3.1 $mgCm^{-2}$ added. The lowest response is shown on bentonite with a linear response achieving 0.4 $mgCm^{-2}$ sorbed for 3.0 $mgCm^{-2}$ added.



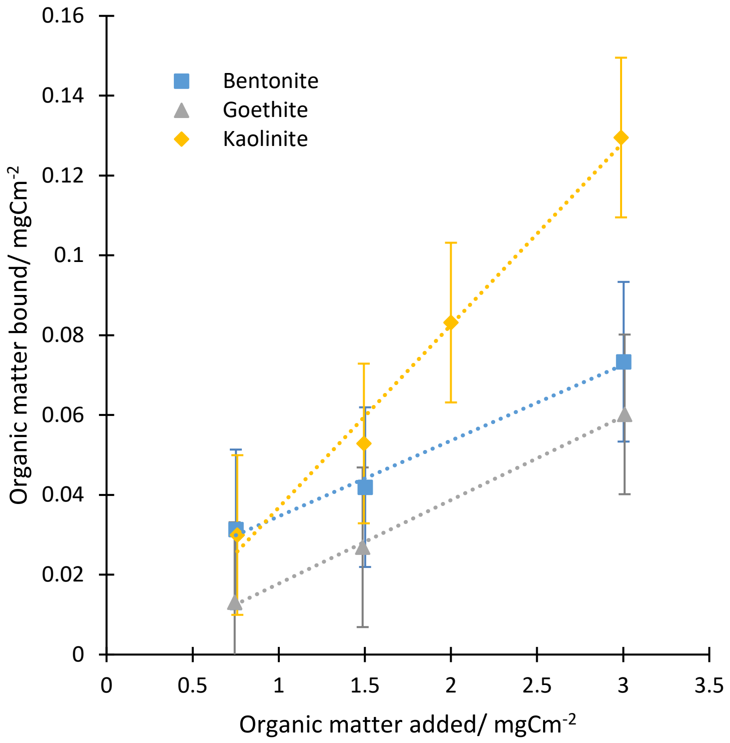
Mineral	Line of best fit	R^2 value
Bentonite ■	y = 0.1352x + 0.0173	$R^2 = 0.99$
Goethite ▲	Non-linear response	
Kaolinite ◆	y = 0.179x + 0.027	$R^2 = 0.75$

Figure 5.5. Sorption of octadecanamide to different minerals.

Octadecanamide was shown in Chapter 4 to interact with kaolinite via hydrophobic interactions. Therefore, the expected sorption preference is kaolinite > bentonite > goethite as in anthracene. However, although the two clays are in this order the greatest sorption is seen to goethite. This may be due to the additional hydroxyl groups in the goethite promoting ligand exchange in octadecanamide- goethite binding. The presence of a nitrogen lone pair on the octadecanamide means this is a viable mechanism and would account for why the interactions with the goethite will be greater than those with the clay.

5.3.6 Stearic acid

A linear response is shown in all three minerals with kaolinite achieving the greatest sorption at 0.13 $mgCm^{-2}$ for 3.0 $mgCm^{-2}$. Bentonite shows the next highest at 0.07 $mgCm^{-2}$ and goethite the lowest at 0.06 $mgCm^{-2}$ both at 3.0 $mgCm^{-2}$.



Mineral	Line of best fit	R^2 value
Bentonite ■	y = 0.019x + 0.0156	$R^2 = 0.99$
Goethite ▲	y = 0.0209x - 0.0032	$R^2 = 1.00$
Kaolinite ◆	y = 0.0457x - 0.0089	$R^2 = 0.99$

Figure 5.6. Sorption of stearic acid to different minerals.

Both anion exchange and hydrophobic interactions were determined to be the sorption mechanism to kaolinite in Chapter 4. If anion exchange was the main mechanism in all three minerals, then the expected sorption preference would be the same as seen for hexadecanol (goethite > bentonite> kaolinite). However, the preference seen here is consistent interactions occurring by Van der Waal interactions and hydrophobic interactions. An explanation for this could be the electrostatic repulsion between the minerals and the stearic acid. Stearic acid has a pKa of 4.75 and is therefore negatively charged at the experimental conditions of pH 9. The point of zero charge of all 3 minerals would mean that at this pH they would all also be negatively charged (Ioannou et al., 2013) , but kaolinite will have the lowest net charge which may explain the greater sorption shown to kaolinite (Satterberg et al., 2003).

5.3.7 Comparison of minerals

Results of the kaolinite experiments were discussed extensively in Chapter 3 and are presented again in *Figure 5.7* for comparison with the other two minerals.

Bentonite results are presented in *Figure 5.8*. As in kaolinite, the two aromatic compounds show the greatest sorption. However, hexadecanol then shows the next greatest sorption, indeed at low concentrations it appears to show greater sorption than the aromatic compounds before plateauing, this may be due to bentonite's higher anion exchange capacity allowing more hexadecanol to interact. However, the plateauing effect suggests these sites are still limited. Octadecanamide, stearic acid and heptadecane show a similar sorption relative to the other compounds as in kaolinite.

Goethite results are shown in *Figure 5.9*. As in both clay minerals the highest sorption is shown by the two aromatic compounds, although carbazole shows greater sorption than anthracene possibly due to carbazole interacting via ligand exchange. Poor sorption is again shown by heptadecane and steric acid, likely due to lack of functionality and electrostatic repulsion, respectively. As in bentonite, hexadecanol shows greater sorption, likely due to goethite's higher anion exchange capacity, although the error in second data point means it is unclear whether this is a linear or plateauing. Octadecanamide binding is greater than in both clays possibly due to the proposed change of interaction mechanism from hydrophobic to ligand exchange.

Overall, the six compounds responded very similarly in all three minerals with the exception of hexadecanol, which showed much greater sorption in bentonite and goethite. This may be due to the more specific nature of the interactions with hexadecanol interacting via anion exchange and therefore more effected by the anion exchange on the different minerals. Indeed, the interaction on bentonite in particular with an initially steep gradient followed by a plateau is indicative of a stronger interaction at a more limited number of sites.

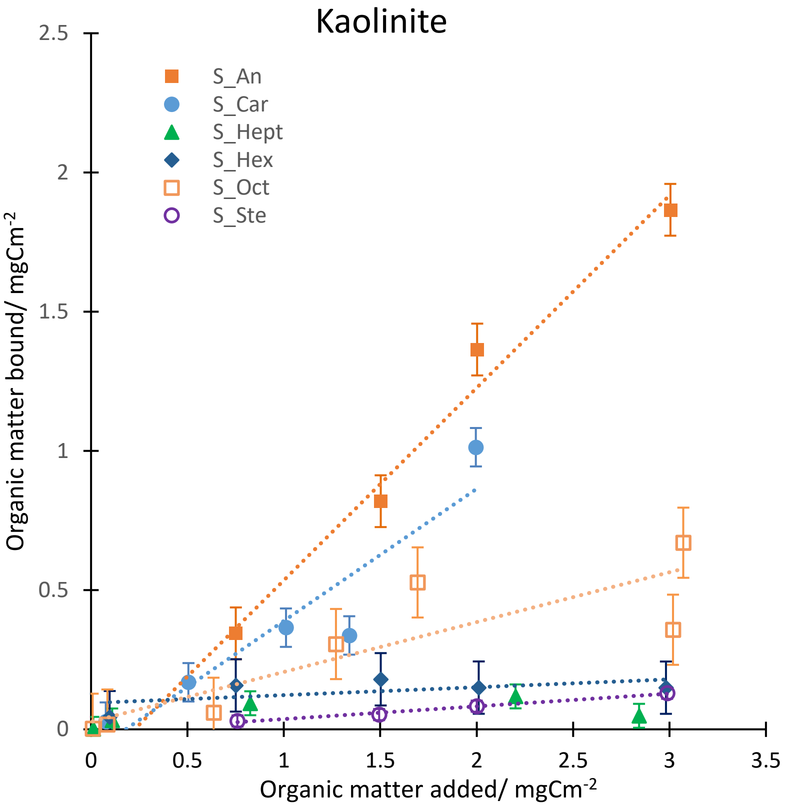


Figure 5.7. Sorption of six standards to kaolinite.

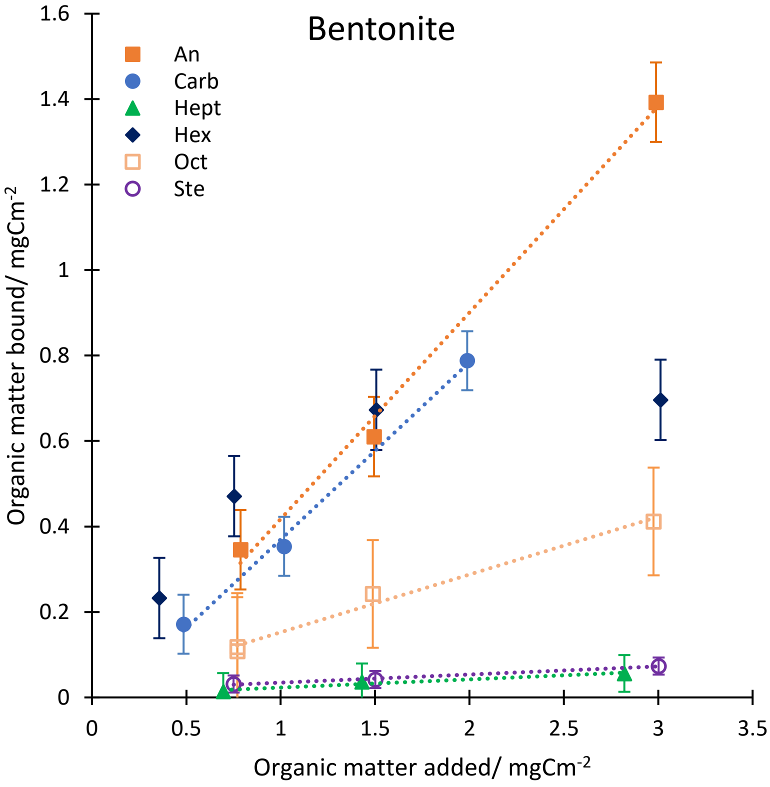


Figure 5.8. Sorption of six standards to bentonite.

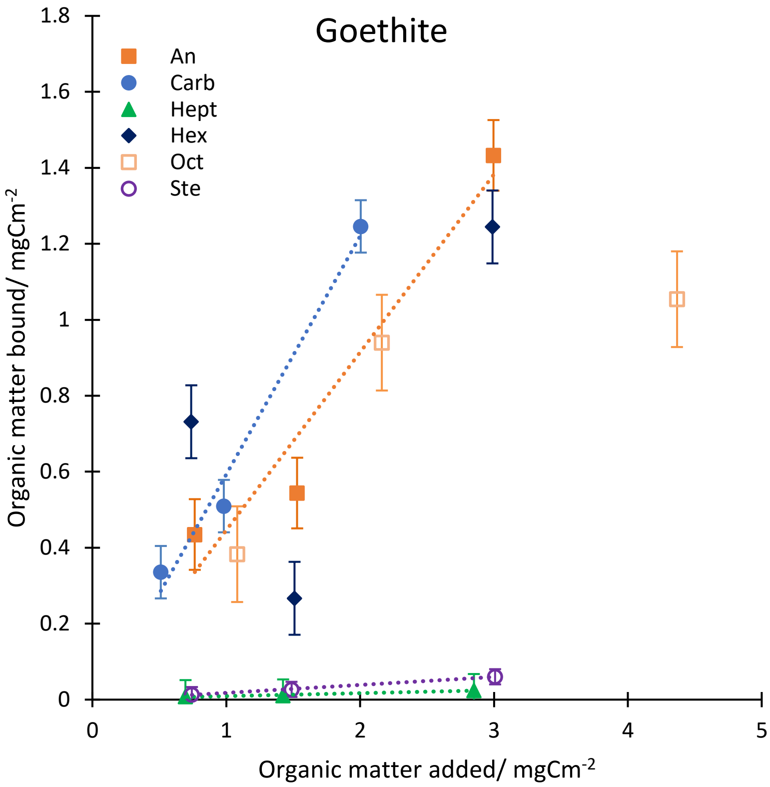


Figure 5.9. Sorption of six standards to goethite.

5.4 Conclusions

The interactions of six organic compounds with three minerals, kaolinite, bentonite and goethite, were investigated. This study suggests that the nature of the organic matter has the greatest impact on sorption, and that the different minerals have minimal impact on which compounds are sorbed the most. In all three minerals, the aromatic compounds showed the greatest sorption, with the highest sorption achieved by anthracene onto kaolinite. The mechanisms determined in Chapter 4 correlate well with the mineral preferences shown by each compound, suggesting that this might be a useful method of predicting interactions with different minerals. It is also interesting to note that the mineral preferences suggest similar mechanisms are operating in all three minerals.

Previously, a preference for iron minerals over clay minerals has been observed (Mikutta et al., 2007). However, this study showed the greatest sorption in kaolinite. Two key differences between the previous study and the current study should be noted. Firstly, as in Chapter 4, the organic matter used in this study was insoluble and hydrophobic, whereas Mikutta et al. (2007) used dissolved organic matter. This means whereas in this study Van der Waal and hydrophobic interactions dominated, compounds are more able to interact via ligand exchange during sorption to goethite in Mikutta et al. (2007). Secondly, the previous study was carried out under conditions found in soils as opposed to marine sediments, for example, at pH 4. At pH 4, goethite will be positively charged which may make a considerable contribution to its increased interaction with predominately negatively charged organic matter.

The importance of iron to organic matter preservation was recently highlighted by Lalonde et al. (2012) demonstrating that over 20% of organic matter in marine sediments may be bound to iron. However, sorption experiments under marine conditions have tended to focus on clay minerals. Interactions with iron minerals can be complicated by iron's redox ability, allowing it to promote both degradation as well as preservation. A recent study has also shown interaction with iron may differ for organic nitrogen compared with organic carbon (Barber et al., 2014). Further investigation into organic matter sorption to iron minerals is therefore required. However the results from this study suggest that under the high pH conditions of marine sediments iron oxides may behave in a fashion more similar to clays than in soils.

Chapter 6 Sorption of functionally defined dissolved organic matter is affected by salinity, mineral type and mass

This chapter is in preparation for submission to Organic Geochemistry as: Elizabeth S. Marsden, Edwin C. Rowe, Inma Lebron, Dan J. Lapworth. Martin Palmer & Jessica Whiteside 2019. Sorption of functionally-defined dissolved organic matter is affected by salinity, mineral type and mass. *Organic Geochemistry.* Work was carried out during a 3 month period spent at the Centre for Ecology and Hydrology, in Bangor, Wales. Elizabeth Marsden carried out experimental design, sample collection, sorption experiments, laboratory and data analysis as well as manuscript writing and editing. Ed Rowe provided advice on experimental design, assistance in data analysis and comments and assistance in the writing of the manuscript. Inma Lebron provided advice on experimental design, training on the use of Laboratory instruments and comments and assistance in the writing of the manuscript. Nathan Callaghan assisted in sample collection. Dan Lapworth carried out the fluorescence spectroscopy and comments and assistance in the writing of the manuscript. Jessica Whiteside and Martin Palmer both provided assistance upon return to Southampton on the writing of the manuscript.

6.1 Abstract

The nature of dissolved organic matter (DOM) flux from land to ocean is a major uncertainty in models of the global ocean budget and global carbon cycle. In particular, the extent to which riverine DOM fluxes are modified by estuarine processes is poorly understood. Laboratory experiments were conducted to test the hypothesis that mineral-DOM interaction is sensitive to salinity changes during estuarine mixing, exerting influence on the flux of DOM from land to ocean. The dependence of this process to specific types of DOM was assessed using DOM derived from three different sources: surface soil organic-rich horizons, subsoil horizons, and marine algal cultures. The influence of the mineral phase was assessed using 1:1 and 2:1 clays and a natural mixture of soil minerals from a North Wales soil. Results indicate that adsorption of DOM onto the minerals was ~10% greater under saline conditions than in fresh water; the mixed assemblage of soil minerals sorbed more DOM than the pure clay minerals and the different DOM types had a minimal effect on the degree of sorption. These results suggest that Van der Waals interactions and cation bridging play an important role in DOM adsorption because these processes are

promoted by increased ionic strength of more saline waters, in particular for higher valency cations. Simplification of the factors determining organic matter-mineral interactions in riverine DOM transport can facilitate its inclusion into Earth system models, allowing more accurate predictions of future changes to the global carbon cycle.

6.2 Keywords

DOM, Sorption, Clay, Organic matter, Estuarine

6.3 Introduction

The transport of dissolved organic matter (DOM) in rivers links together three of the world's important carbon pools: soils, ocean, and atmosphere (Meyersschulte and Hedges, 1986, Li et al., 2017). Among other factors, the magnitude of this flux is hypothesised to be controlled by the nature of the DOM, interactions of DOM with mineral surfaces and changes in physico-chemical conditions at the land-sea interface during estuarine mixing (Jin and Zimmerman, 2010, Meyersschulte and Hedges, 1986, Sholkovitz, 1976). The importance of these processes in absolute and relative terms is, however, poorly understood (Ciais et al., 2013). As a result, land-ocean carbon transfer is not explicitly included in most global carbon cycle models (Ciais et al., 2013).

Previous studies identified three key factors in DOM-mineral interactions: DOM type, mineral type and environmental conditions (Keil and Mayer, 2014, Arnarson and Keil, 2000). Many of these studies have concluded that the nature of the organic matter plays an important role in determining the degree of DOM-mineral interaction, with the composition in terms of functional groups and the molecular mass of the organic matter determining the extent of sorption (Arnarson and Keil, 2000, Swenson et al., 2015, Kang and Xing, 2008, Ahmat et al., 2016, Aufdenkampe et al., 2001). Different classifications of DOM characteristics, such as molecular weight (Arnarson and Keil, 2000), photic properties (Ding and Shang, 2010), aromaticity (Mikutta et al., 2007), functional groups (Swenson et al., 2015, Lu et al., 2010, Liu and Lee, 2006, Kang and Xing, 2008, Ahmat et al., 2015, Aufdenkampe et al., 2001) and DOM source (Satterberg et al., 2003), mean that comparisons between different studies remain difficult. This is partly caused by the fact that complete characterisation of all these properties in a single study is time-consuming and expensive, hence it is often useful to define the functional classes of DOM using easily measurable characteristics, such as source and optical properties (Anderson et al., 2019).

While most studies suggest that the nature of the mineral phase appears to be of secondary importance in determining the extent of DOM-mineral interaction, the surface charge of the mineral does play a role. For example, minerals with positive surface charges, such as calcium carbonate, show a preference for negatively charged DOM components (Aufdenkampe et al., 2001, Carter, 1978), and iron minerals and clays have also been shown to interact strongly with DOM and provide protection from degradation (Saidy et al., 2015, Drouin et al., 2010, Ransom et al., 1997, Dumig et al., 2012).

The term "clay" can be ambiguous, and may refer to either the smallest particles, typically defined in sedimentology as < 4 µm (although in soil science often < 2 µm is used), or to a specific defined class of aluminosilicate minerals (Allaby, 2008). Aluminosilicate clay minerals are a major component of soils and sediments and have been widely used in laboratory studies (Meier et al., 1999, Drouin et al., 2010, Saidy et al., 2015) and their concentrations in soil and sediment samples correlate well with organic matter abundances (Dumig et al., 2012, Kennedy and Wagner, 2011). The role of non-aluminosilicate minerals within the clay size fraction is, however, less clear. The < 4 µm size fraction of non-aluminosilicate minerals will also likely have a high surface area, but other surface properties, such as surface charge, are likely to be different from clay minerals *sensu stricto*.

In addition to the nature of the DOM and mineral, environmental conditions such as pH, salinity and ionic composition (Arnarson and Keil, 2000) are also important in determining the extent of DOM-mineral interactions. Changes in salinity play a particularly important role in DOM-mineral interaction and transport during passage of DOM from fresh rivers through estuaries and into coastal ocean settings. For example, increasing salinity can lead to the flocculation of different types of particles, impacting the concentrations of both dissolved inorganic species and dissolved and particulate organic matter (Sholkovitz, 1976), with both increased and decreased adsorption being reported for various DOM and inorganic species (Arnarson and Keil, 2000, Henrichs and Sugai, 1993, Wang and Lee, 1993). Hence some of the studies reporting removal of DOM from solution during estuarine mixing (Arnarson and Keil, 2000) may reflect DOM flocculation rather than DOM-mineral sorption. The effects of changing salinity are further complicated by the presence of different components within seawater. For example, the presence of divalent cations and complexing anions such as sulfates can both promote and inhibit different bonding mechanisms. Hence, further investigations of the effects of salinity on sorption of different DOM sources are required to address these uncertainties. In this study the interactions among three types of DOM and three mineral sources (*Table 6.1, Table 6.2*) at riverine salinity (0.01-0.08 g total salts kg^{-1} water) and marine salinities (30 g total salts kg^{-1} water), in an incubation experiment were investigated.

Table 6.1. Description and source of Dissolved Organic Matter to be used in this study.

Organic matter	Description	Examples
DOM T1	Strongly UV absorbing, younger, more coloured, more reactive terrestrial organic matter. Prone to photooxidation and flocculation, but less susceptible to microbial degradation, typically released from topsoils.	Lignin and other structural compounds from an upland source.
DOM T2	Weakly UV absorbing, older, less reactive, and less coloured terrestrial organic matter. That prone to microbial degradation but less susceptible to photooxidation and flocculation, released from baseflow.	Carbohydrates and proteins and compounds derived from arable soils, included man-made DOM such as sewage
DOM A	Aquatically produced DOM produced via phytoplankton exudation, zooplankton grazing and detritus turnover. These compounds are not susceptible to photo oxidation but are semi labile with a turnover of weeks to months.	Fatty acids, sugars, amino acids and terpenoids

Table 6.2 Description of minerals to be used in this study.

Mineral	Description
Kaolinite	1:1 clay
Bentonite	2:1 clay
'Bangor' Soil	soil sample exhibiting greater variation in particle size and mineralogy
Mineral-free blanks	a control for other factors leading to a decrease in dissolved organic carbon, such as degradation and/or flocculation

This experimental approach allowed the testing of the following hypotheses:

H1: DOM type A is expected to experience the greatest sorption, due to its high nitrogen content, because nitrogen-rich organic matter has been shown to be preferentially sorbed (Aufdenkampe et al., 2001). DOM type T1 is expected to show the next greatest amount of sorption because it contains larger molecules and it has had reduced previous exposure to mineral surfaces than type T2. Both these factors have been identified as resulting in increased mineral interactions (Aufdenkampe et al., 2001, Arnarson and Keil, 2000).

H2: Of the different mineral types, the two clays are expected to achieve the greatest sorption. Bentonite is a 2:1 clay, and has a higher overall surface charge and greater cation exchange capacity, is likely to sorb more than kaolinite (Satterberg et al., 2003). The lowest extent of sorption is expected by the mixed soil material because it has a lower aluminosilicate clay content (see below). For all three mineral types it is anticipated that increasing the ratio of mineral mass to DOM will increase the amount of DOM sorption because this will provide additional surface area. The final treatment is a mineral-free sample and serves as a control. It is anticipated that this control is likely to show very little or no change in DOM concentration during the experiment. Any change that is observed will be likely due to degradation or flocculation of the DOM.

H3: Increased salinity is expected to lead to an increase in DOM sorption because the higher salinity will provide more cations for cation bridging, which is an especially important mechanism for enhancing clay-organic matter interactions (Arnarson and Keil, 2000).

6.4 Materials and methods

6.4.1 Materials

Kaolinite was obtained from Fischer Scientific as pure kaolin. The composition as determined by X-ray diffraction (XRD) was 72.9% kaolinite, 23.8% illite and 6.3% quartz. Bentonite was obtained from the British Drug Houses Ltd, BDH laboratory Chemicals Division, Poole and had an XRD composition profile of 89.1% montmorillonite (swelling clay), 9% albite, 1.9% quartz. Bangor Soil, collected from Pontbren, near Llanfair Caereinion, Wales, had an XRD-determined composition of 44.6 % illite, 35.3 % quartz, 10 % smectite, 8 % albite, 2.1 % chlorite, and a clay-sized fraction of 39.9 ±7.8. Previous studies have suggested that the non-clay sized fraction of the solid phase has a minimal effect on sorption (Bock and Mayer, 2000, Wiseman and Puttmann, 2006, Ransom et al., 1997), therefore mineral matter was added to give an approximately equal mass of clay-sized particles, i.e. 2.5 x the mass of Bangor soil was used compared to masses of kaolinite and bentonite.

Prior to the experiments, the minerals were heated to 400 °C to remove any pre-existing organic matter. After heat treatment, surface area measurements were 16.3 $m^2 g^{-1}$, 12.4 $m^2 g^{-1}$ and 18.3 $m^2 g^{-1}$ for kaolinite, bentonite and Bangor soil, respectively.

The DOM sample dominated by T1 (more coloured and photolabile) was collected from Nant y Brwyn (longitude: -3.802°, latitude: 52.988°), an undisturbed upland peat stream in Snowdonia, Wales. The DOM sample dominated by T2 was collected from the Plas Uchaf reservoir (longitude: -3.546°, latitude: 53.229°), near to St Asaph, Wales, a more arable setting. The organic matter representing autochthonous DOM, i.e. type A, was produced by the marine phytoplankton *Tetraselmis suecica,* which was grown nonaxenicily at 20 °C on a 12h:12h light:dark cycle, bubbled continuously with 0.2 µm filtered air, in Walne's Medium. The phytoplankton cells were harvested during the exponential growth stage by centrifugation followed by freeze drying. A suspension of 0.33 g L^{-1} in deionised water was then prepared and shaken for 17 hours to allow dissolution of the more soluble organic compounds.

6.4.2 Instrumentation

Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) measurements were performed using a Thermalox 5001.03, from Analytical Science. Solutions were acidified, sparged with oxygen to remove carbonate, and calibrated with a 7 point calibration curve. Each sample was injected four times with an injection volume of 40 µL, average coefficient of variance was 4 % for carbon and 6 % for nitrogen. Samples above a coefficient of variance of 20 % were repeated. Specific electrical conductivity (SEC) was measured with a Jenway 4320 and the pH with a Metrohm Titrando with an Aquatrode +Pt 1000 pH electrode. Anion and cation contents were determined on a Metrohm 930 compact IC flex ionic chromatograph, using a 7 point calibration curve.

Fluorescence Excitation-Emission Matrix (EEM) was used to determine the previously mentioned DOM classifications (Lapworth et al., 2008). A Varian™ Cary Eclipse fluorescence spectrometer was used for the fluorescence analyses. Excitation (Ex) wavelengths were set between 200 and 400 nm with a 5 nm bandwidth and emission (Em) wavelength set between 250 and 500 nm with a 2 nm bandwidth. The scan rate was 9600 nm min^{-1} and the PMT voltage was 725 V. Quartz cells with a 1 cm path length were used. Ultrapure water (ASTM type I reagent grade water, including a UV cracker) was used for the blank samples and to clean the quartz cell between samples. All the post processing of the fluorescence data, the blank and the absorbance correction, was carried out using the R statistical package (R-Team, 2008, Lapworth and Kinniburgh, 2009).

The multivariate technique Parallel Factor Analysis (PARAFAC) was used to evaluate and characterize the complex mixtures of fluorescent DOM (fDOM) fractions, which has commonly been employed in past studied in environmental waters (Bro, 1997). This method decomposes the combined fluorescence signal into individual, distinct modelled components (Bro, 1997, Murphy et al., 2013, Stedmon et al., 2003). EEM-PARAFAC models the three-way (excitation, emission, intensity) EEM data using fitting routines to minimise the sum of squares of the residuals (Stedmon and Bro, 2008). The ‘DOMFluor v1.7’ toolbox (Stedmon and Bro, 2008) was used to undertake this analysis, explore the data set and validate the PARAFAC modelling. A three fDOM components component model was validated using independent split-half analysis of the data set, following removal of outliers (Stedmon and Bro, 2008). The inclusion of further components could not be validated, and the three component model explained 99.5% of the variability in the absorbance corrected EEM data. The three components identified were: Component 1 (C1, Ex/Em: 245-380/416-462 nm), component 2 (C2, Ex/Em: 245-345/372-444 nm) and component 3 (C3, Ex/Em: 245-315/314-376 nm). Based on previously reported distributions of Em/Ex these components have been assigned as: C1 humic-like, C2 fulvic-like, C3 tryptophan-like (Coble, 1996, Chen et al., 2003). Other DOM characteristics were investigated through the use of two further indices: (i) the fluorescence index (FI), which is commonly used to differentiate between terrestrial and microbial DOM sources (McKnight et al., 2001), and (ii) the humification index, an indication of humicity, and the condensing of fluorescing molecules (Zsolnay, 2001). The fluorescence indices shown in *Table 6.3*, are all low in microbial organic matter but variation is consistent with three different sources. The humification index indicates A is the least degraded and T1 is a little more degraded than T2. The EEM results also suggest a differing chemical make-up with different proportion of the three different components. Characterisation of the three DOM types can be seen in *Table 6.3*.

The mineralogy of the solid phases was determined by X-ray diffraction (XRD) using a Panalytical X'Pert pro diffractometer machine fitted with a Cu X-ray tube, operating at 35 kV, 40 mA utilising automatic slits and a step size of 0.02º 2θ at 1 second/ step. Semi-quantitative analysis was undertaken using a least squares method similar to that used in the Microsoft Excel-based programs RockJock (Eberl, 2003), and FULLPAT (Chipera and Bish, 2002). Surface areas were determined with nitrogen absorbance using the Brunauer-Emmett-Teller (BET) method on a Micromeritics 3 flex 3.02 at 77 K.

Table 6.3. Properties of dissolved organic matter (DOM) solutions consisting predominately of T1, T2 and A types, showing Dissolved Organic Carbon (DOC), Total Dissolved Nitrogen (TDN), pH and conductivity, together with a number of fluorescence-derived indexes. The fluorescence index (FI), which is commonly used to differentiate between terrestrial and microbial DOM sources (McKnight et al., 2001), and (ii) the humification index, an indication of humicity, and the condensing of fluorescing molecules (Zsolnay, 2001). Parallel Factor Analysis (PARAFAC)(Bro, 1997) was used to separate the excitation, emission matrix into 3 components, assigned as: 1 humic-like, 2 fulvic-like and 3 tryptophan-like (Coble, 1996, Chen et al., 2003) whose relative concentrations are presented in Raman units.

Sample	**T1**	**T2**	**A**
DOC mg L^{-1}	14.63	14.30	5.80
TDN mg L^{-1}	0.37	1.96	0.57
Specific Electrical conductivity µS cm^{-1}	24.5	153.4	24.5
salinity	0.019	0.076	0.019
pH	5.65	7.3	6.48
Florescence index	1.04	1.23	0.87
Humification index 2	0.92	0.89	0.48
EEM humic Fmax/ RU	3.45	1.87	0.245
EEM Fulvic Fmax/ RU	4.87	3.12	1.11
EEM trypophan Fmax/ RU	0.31	0.20	0.57

6.4.3 Sorption experiments

Each mineral type was exposed to each of the three types of DOM under both saline (salinity 30) and riverine (salinity 0.01-0.08) conditions. For the kaolinite and bentonite mineral types, different mineral-mass treatments were used, with 20, 40 and 80 mg of clay. For the Bangor soil, masses of 50, 100 and 200 mg were used to account for the clay size fraction being 39.9%. These mineral loading are typical of mineral loading found in rivers (Aufdenkampe et al., 2001). Each combination of factors was repeated three times, giving a total of 216 incubations. Mineral free controls were used to determine decreases in DOC concentration in solution resulting from respiration or interactions with the centrifuge tube, giving $DOC_{control}$.

For the incubations, the starting DOM solutions were first adjusted to the required salinity. For riverine samples no adjustment was required. For marine samples artificial sea salt (Subov, 1931) was added to adjust EC to give a salinity of 30. These solutions were then allowed to stand for 15 minutes before being filtered through GF/C filters with a nominal pore size of 0.45 µm. Three aliquots of this starting solution were then set aside to measure $DOC_{initial}$. Then 30 mL of DOM solution was added to a centrifuge tube containing the appropriate mass of mineral. Tubes were shaken for 2 hours before being filtered through Whatman GF/C filters (0.45 µm) prior to analysis by DOC, giving DOC_{final}. Analysis was generally conducted within 3 hours, where this was not possible samples were stored at 4 °C and analysed within 24 hours. Storage at this temperature has previously been shown to reduce any degradation to below detectable level for these timescales (Peacock et al., 2015).

The percentages of organic carbon sorbed to the mineral phase was determined according to Equation 3.

Equation 3.

$$\%DOC_{sorbed} = \frac{DOC_{control} - DOC_{final}}{DOC_{control}} \times 100$$

The extent of DOC sorption was evaluated by analysis of variance, using the lm function (from the stats package) within the R programming language (version 3.3.3), with DOC sorption as a response, and mineral mass (continuous), DOM type, mineral and salinity (discrete) as explanatory variables (see *Table 6.4* for levels). Model simplification was carried out on general linear models, starting with the most complex model (including a 4-way interaction). Model terms (variables and/or their interactions) were removed in a stepwise fashion, each time using analysis of variance to check for significant changes in model deviance. Tukey HSD from the agricolae R package was also used to compare which variables within a factor were significantly different.

6.5 Results

DOC concentrations were changed by exposure to minerals, with mean DOC sorption of 8% and a p value of <0.001. The results of the minimum adequate model are shown in Table 6.4 together with the p value for each factor.

Table 6.4. Analysis of variance of minimal adequate model for percentage sorption of dissolved organic carbon.

Factor	Degrees of freedom	F value	*p* value
Salinity	1	41.3	< 0.001
DOM type	2	0.614	n.s.
Mineral type	2	6.65	< 0.01
Mineral mass	1	47.4	< 0.001
Salinity x Mineral type	2	7.97	< 0.001
DOM type x Mineral type	4	3.83	< 0.01
Mineral type x Mineral mass	2	4.05	< 0.05
Residual	147		

The minimum adequate model showed that the factors with greatest effect on sorption were mineral mass and salinity, with P values less than 0.001, followed by mineral type with a P value of less than 0.01 and the two-way interactions. Of the two-way interactions the greatest effect is had by salinity and mineral type with a P value less than 0.001 followed by DOM type and mineral type with a P value of less than 0.01, then mineral type and mineral mass with a P value less than 0.05. Organic matter type shows the smallest effect on sorption, as an individual factor it is not significant only having a significant effect in combination with mineral mass.

Organic matter type not having a significant effect on the percentage of DOC sorbed contradicts hypothesis one. In contrast, both the amount and the type of mineral had a significant effect. Sorption increased with more mineral mass, and was greatest on Bangor soil followed by bentonite, and finally kaolinite. Significance values for key contrasts within the minimal adequate model are summarised in Table 6.5. Full results can be found in the appendix. These show that only the difference between the Bangor soil and the kaolinite was statistically significant. This result contradicted hypothesis 2, which postulated that the Bangor soil would show the lowest sorption. Salinity also had a significant effect on sorption, with greater sorption occurring at marine salinities. Results also indicate that the difference between all three mineral masses used are significant.

*Table 6.5. Results of tukey tests for the significance between individual treatments *** = p < 0.001; ** = p<0.01; * = p < 0.05; . = p < 0.10.*

Factor	**Difference**	***p* value**	**Significance**
Salinity			
Marine - Riverine	6.429941	0	***
DOM type			
Algal - Type 1	-0.19848	0.9856	
Algal - Type 2	1.06433	0.661	
Type 1 - Type 2	1.26281	0.5589	
Mineral type			
Bangor soil - Bentonite	1.626342	0.3825	
Bangor soil - Kaolinite	4.419841	0.0012	**
Bentonite - Kaolinite	2.793499	0.0619	.
Mineral mass			
20-40	-5.25821	1.00E-04	***
20-80	-8.78918	0	***
40-80	-3.53097	0.0126	*

As well as the main factors, the analysis of variance also shows significant two-way interactions which are illustrated in the box plots below. *Figure 6.1* showing salinity and mineral type and illustrates how salinity has a much greater impact on bentonite than the other two minerals, with the difference between BR and BM, greater that that between KR and KM or SR and SM. The effect of organic matter type and mineral type is shown in *Figure 6.2* which illustrates the minimal difference between the different organic matter types even on different minerals, only T1 on Bangor soil shows a notably higher mean value. Mineral type and mineral mass are illustrated in *Figure 6.3*, as well as illustrating that greater sorption is achieved by all minerals at higher masses, the trend of Bangor soil showing the greatest sorption followed by bentonite and then kaolinite can be seen to get stronger at the higher mineral mass.

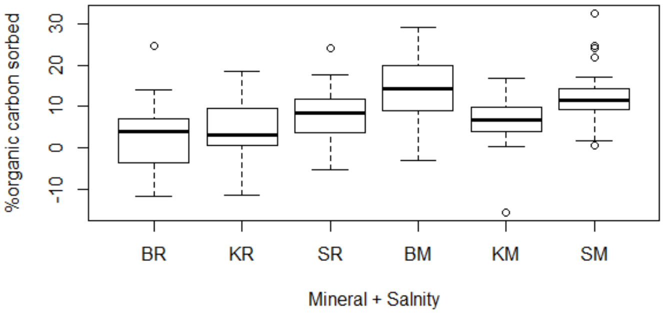


Figure 6.1. Effect of mineral type and salinity on the percentage sorption of dissolved organic carbon (mean for different types of dissolved organic matter and mineral mass). The first letter is indicative of the mineral: B- bentonite, K- kaolinite, S- Bangor Soil. The second letter indicates the salinity: R-riverine, M-marine. Each box plot represents 27 data points.

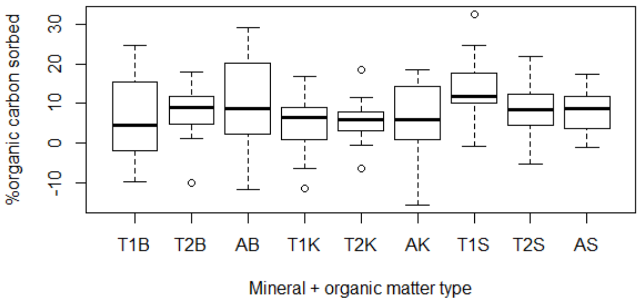


Figure 6.2. Effect of organic matter type and mineral type on percentage sorption of dissolved organic carbon (mean for different salinities and mineral mass). The first letter is indicative of the organic matter and the second the mineral: B- bentonite, K- kaolinite, S- Bangor Soil. Each box plot represents 18 data points.

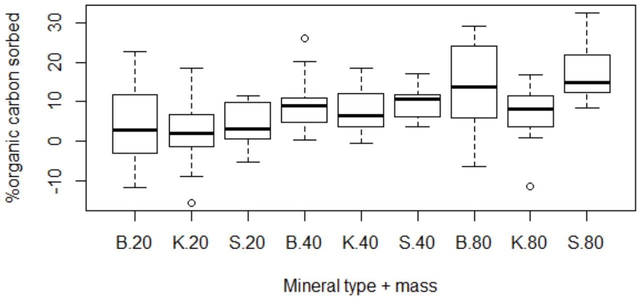


Figure 6.3. Effect of mineral type and mineral mass on percentage sorption of dissolved organic carbon (mean for different salinities and organic matter type). The letter is indicative of the mineral: B- bentonite, K- kaolinite, S- Bangor Soil and the number the mass of clay-sized particles in mg. Each box plot represents 18 data points.

The significance of the two-way organic matter and mineral type interaction suggests that organic matter type does have some importance at least within one of the mineral types. Tukey results revealed only one contrast with (marginal) significance, between DOM type T1 and A on Bangor soil, with a P value of 0.0592 (see appendix). Of the three two-way interactions, the organic matter and mineral type interaction had the smallest F value (*Table 6.4*) suggesting that the interaction between mineral mass and salinity is more important to consider.

6.6 Discussion

Results showed that the factors with greatest effect on sorption were mineral mass and salinity, followed by mineral type and the two-way interactions, with organic matter type having the smallest effect on sorption. The increased sorption with increased mineral mass is likely to be due to the increased mineral surface area that this provided. The difference in sorption of DOM by one mineral relative to another is small and does not correlate with the surface area of the minerals. The mineral surface areas were 12.4 m² g^{-1}, 16.3 m²$g^{-1}$and 18.3 m^2 g^{-1} for bentonite, kaolinite and Bangor soil, respectively. Whilst the Bangor soil showed the greatest sorption and had the greatest surface area, kaolinite had a greater surface area than bentonite, but bentonite showed greater sorption. This may be because organic matter has been shown not to be present on mineral surfaces in a uniform layer, despite some studies having suggested a constant ratio of organic matter to mineral surface area (Mayer et al., 1985, Weiler and Mills, 1965, Tanoue and Handa, 1979) . Organic matter binds at specific locations (Ransom et al., 1997, Mayer, 1999, Arnarson and Keil, 2001), and the ratio of sorption sites to surface area is likely to vary between different minerals. Indeed, montmorillonite (a major component of bentonite) has been shown to have a higher sorption capacity than kaolinite, and the high sorption in the Bangor soil may also be due to the presence of iron which has been shown to significantly increase DOM sorption capacity, as well as the soil's higher surface area (Satterberg et al., 2003, Lalonde et al., 2012, Kaiser and Guggenberger, 2000, Zhang et al., 2013, Wang et al., 2013).

Previous work has noted the increased sorption of DOM by minerals at higher salinity (Arnarson and Keil, 2000, Sholkovitz, 1976, Meyers and Quinn, 1973). Mineral flocculation, particularly of bentonite, has been shown to increase significantly at higher salinities (Baik and Lee, 2010), which seems likely to reduce the availability of the mineral surface for organic matter sorption (Meyers and Quinn, 1973). However, the presence of bound organic matter has been found to noticeably reduce this flocculation effect (Heil and Sposito, 1993). Suppression of anion and cation exchange, reducing organic matter sorption by these mechanisms, is caused by increased competing anions and cations and the suppression of ligand exchange by elevated sulphate concentration. As sorption in this study is increased by increased salinity, it is unlikely these are the main sorption mechanisms occurring here.

The positive correlation between the extent of DOM sorption and salinity most likely results from increased weak short-range Van der Waal interactions and cation bridging. Van der Waal interactions require that the sorbed compounds closely approach the mineral surface. At lower salinity this is impeded by a larger double layer (a section of counter ions close to the mineral surface) through which the DOM would have to pass. With increased ionic strength at higher salinities, the size of the double layer decreases and the DOM is able to more readily approach the mineral surface. This effect is greatest in bentonite, which is the most highly charged mineral considered here (Zadaka et al., 2010), and which is consistent with our results (*Figure 6.1*). The presence of increased concentrations of divalent cations also increases the extent of cation bridging. This process allows the negatively charged organic matter to bind to negatively charged minerals via bridging cations. In the case of bentonite, cation bridging allows the negatively charged face sites to sorb DOM, in addition to the positively charged edge sites, increasing the number of potential sorption sites.

The relatively low importance of DOM type in determining the degree of sorption was unexpected. Previous studies have found that the DOM source affects sorption more than mineral type e.g. (Satterberg et al., 2003); however, it should be noted that many of these studies were conducted with a much lower organic matter: mineral ratio, < 0.2 mg C m^{-2} (Drouin et al., 2010, Satterberg et al., 2003) than was the case in this study, where the ratio varied in the range 0.12-1.77 mg C m^{-2}. Other works on organic matter degradation have demonstrated that when the mineral was present in excess, the degree of protection from degradation that the mineral afforded was determined by the strength of the organic matter-mineral interaction. This interaction is a function of both the mineral and organic matter types. In contrast, when the organic matter was in excess, 33.3 $mgCm^{-2}$ on kaolinite, the degree of protection was determined by the mineral surface area (Saidy et al., 2015, Saidy et al., 2013). That might explain the observed importance of mineral mass in this study which is strongly correlated to mineral surface area.

Within marine sediments there appears to be a relatively constant coverage of organic matter of approximately 1.5 mg C m^{-2} mineral surface area (Mayer et al., 1985). The organic matter: mineral surface area ratio in this study varied in the range 0.12-1.77 mg C m^{-2}. Laboratory-based sorption experiments have achieved much lower coverages than 1.5 mg C m^{-2}, which is likely to explain why DOM type was not a significant factor because the organic matter is still likely in excess (Mayer, 1994a, Mayer et al., 1988, Arnarson and Keil, 2000, Drouin et al., 2010). This decreased coverage observed in laboratory studies may result from changes in the sediment structure caused by removal of organic matter prior to the experiment, because this can collapse the overall structure of the sediment and reduce the available surface area (Liu and Lee, 2006). It is also possible that some of the organic matter preservation seen in natural sediments does not primarily originate from mineral interactions, but as a result of other factors such as redox chemistry (e.g., anoxic versus oxic conditions). Therefore, the relative excess of organic matter in relation to suitable sorption sites in this study is likely to be the reason why there was no preference for one organic matter type over another. That said, it is also possible that some selective sorption of specific compounds or functional groups within each DOM type occurs because this would not be detected in the total DOC measurements.

The combined effect of the mineral type and the DOM type on the extent of sorption may be a result of the weaker sorption of type T1 DOM on bentonite and the greater sorption of type T1 DOM on Bangor soil (*Figure 6.2*). In which case, this may be related to the acidic nature of DOM type T1, because acidic organic matter is negatively charged and will therefore interact poorly with the negatively charged bentonite. The increased sorption of DOM type T1 with the Bangor soil may therefore indicate that this mineral type may have more positively charged sorption sites. This could be investigated further either indirectly by extracting the bound organic matter to determine if this is more likely to bind to positive or negative sites, or more directly by using an analytical technique to visualise the bound organic matter in situ, such as solid state NMR, transmission electron microscopy or atomic force microscopy.

6.7 Conclusions

This study demonstrates that under mineral loading conditions typical of those found in rivers (Aufdenkampe et al., 2001), DOM-mineral interactions make a significant contribution to the removal of DOM, and therefore are important to include in DOM transport models. It was also shown that the DOM: mineral surface area ratio is an important determinant because it gives an indication of which factors will have the greatest effect on the amount of sorption observed. At the concentrations used in this study, the nature of DOM source had a minimal impact on the degree of sorption. This suggests that if required, removal models could potentially be simplified by the exclusion of DOM type as a factor in mineral interaction. However, mineral mass and type need to be included because they have an important effect on the amount of sorption. It is also important to consider the influence of flooding events that lead to large suspended sediment loads within rivers, which may cause the DOM type to become the limiting factor. Further laboratory studies are needed to determine the exact DOM: mineral ratio at which this may occur. At higher mineral concentrations than those used in the current study, it is likely that only the DOM type would need to be considered because mineral type and mass would no longer be limiting, meaning that models of DOM sorption could still be simplified. Under either situation, salinity is an important factor and critical for accurate modelling because higher salinity has been shown to increase sorption. Although further experimental studies are needed, this study indicates that models of DOM-mineral interactions could be simplified due to the minimal or limited influence of DOM type, at least where sediment loads are comparatively small.

6.8 Acknowledgments

The study was funded by the UK Natural Environmental Research Council (grant number NE/L002531/1) SPITFIRE program, and by the UK Natural Environment Research Council under the LOCATE project (grant NE/N018087/1). We would like to thank Dr Nathan Callaghan for his help in collecting organic matter samples and Dr Jennifer Williamson for her input on collection sites. DJL publishes with the permission of the Executive Director of the British Geological Survey, NERC-UKRI.

Chapter 7 Conclusion

Current human activities, such as the burning of fossil fuels and changes in land use, mean that understanding the mechanisms and feedbacks of the global carbon cycle is becoming ever more critical (Friedlingstein, 2015). Preservation of organic matter in marine sediment is important for the removal of carbon dioxide and accumulation of oxygen in the atmosphere (Mackenzie et al., 2004). Past research has identified that mineral interactions are a key part of this preservation process (Hedges and Keil, 1995). Studies have since shown that clays and iron minerals interact most strongly with polar compounds via ligand exchange, cation bridging and Van der Waals interactions. However, a number of questions still remain, such as the reason for the observed monolayer ratio of organic matter to mineral surface area (Mayer, 1999). This study aimed to further understanding of organic matter-minerals interactions in the following ways; firstly, by examining both dissolved and particulate organic matter whilst trying to disentangle the effects of molecular weight and organic matter functionality; secondly, to investigate the impact of organic matter type on the mechanism of interaction. Thirdly, to compare these results in different minerals. Finally, to use natural organic matter to determine the applicability of results in a natural system.

7.1 Role of organic matter type in organic matter-mineral interactions

Separation of bound and unbound particulate organic matter was achieved in this study using centrifugation and density fractionation. This then allowed the inclusion of more hydrophobic compounds particularly aromatic compounds, which have previously been excluded due to their absence from the dissolved fraction (Lu et al., 2010, Newcomb et al., 2017). The use of standards (anthracene, carbazole, heptadecane, hexadecanol, octadecanamide and stearic acid) also allowed the disentanglement of the effects of abundance and mineral preference for one organic matter type over another. This revealed that, in addition to the previously observed bonding preference for nitrogen-containing compounds (octadecanamide in this study), there was an even greater preference for aromatic compounds (anthracene and carbazole in this study). This observation illustrates the importance of including all organic matter types during experimental design. The use of further standards (behenic, stearic, and palmitic acid) also allowed the determinations of the importance of molecular weight to organic matter-mineral interactions, as it was shown that compounds with a higher molecular weight show greater sorption, even in the absence of greater functional groups.

These individual results were complemented by combined experiments, where all the standards were added simultaneously. It was initially anticipated that this would result in competition between the different types of organic matter, with those with the strongest interactions binding first and inhibiting the binding of other compounds. However, sorption for all compounds was notably greater in the combined experiments, with little difference between the amount of sorption for the different compounds. The similarity between the concentrations reached by the combined compounds and the aromatic compounds in the individual sorption experiments, lead to the hypothesis that increased sorption shown was due to the non-aromatic compounds binding to the aromatic compounds, which themselves were binding to the mineral. However, repeating the combined experiment without aromatic compounds still resulted in greatly increased sorption, compared to the individual sorption experiments. Having determined that this result was not due to the increased organic matter concentration forcing organic matter into the solid phase, this shows that increasing the variety of organic matter present leads to increased sorption. Previously, laboratory studies have struggled to obtain the 1.5 $mgCm^{-2}$ seen in marine sediments but in the combined experiments seen here ratios were nearly 10 times this at ~ 12 $mgCm^{-2}$ (Arnarson and Keil, 2000, Drouin et al., 2010). Possible explanations for this include the lack of microbial degradation in this study and higher than natural levels of aromatic compounds. However, it is also worth noting that in soils, organic matter sorption often exceed this ratio (Kaiser and Guggenberger, 2000), and the 1.5 $mgCm^{-2}$ seen in marine sediments may be more indicative of the limited amount of organic matter reaching the sea floor than of mineral saturation.

7.2 Role of mineral and mechanism

Six main mechanisms are important to organic matter-mineral interactions: ligand exchange, cation bridging, anion exchange, cation exchange, van der Waals interactions and hydrophobic effects. Previously, ligand exchange, cation bridging and Van der Waals interaction have been identified as the most important of these mechanisms (Arnarson and Keil, 2000, Feng et al., 2005, Mikutta et al., 2007). This study enabled the determination of the mechanism for individual molecules, and demonstrates the following: anthracene interacted via hydrophobic interactions and Van der Waal forces; carbazole by hydrophobic interactions, Van der Waals forces and ligand exchange; heptadecane by hydrophobic interactions and Van der Waals forces; hexadecanol by anion exchange; octadecanamide by hydrophobic interactions; and stearic acid by hydrophobic interactions and anion exchange. None of the compounds used in this study seemed to be interacting by cation bridging and only carbazole showed any interaction via ligand exchange, despite these being shown to be key mechanisms previously (Mikutta et al., 2007, Arnarson and

Keil, 2000, Feng et al., 2005). Instead more hydrophobic interactions were detected. This is hypothesised to be due to the different nature of the organic matter used here to the organic matter used previously. Previous studies have concentrated on dissolved organic matter which is likely to be more hydrophilic in nature, whereas the organic matter used here is more hydrophobic which explains the increased importance of hydrophobic interactions.

The mechanism of interaction determined for each molecule provided a good indication of the molecule's interaction with different minerals. Those interacting via hydrophobic and Van der Waal interactions bound most to kaolinite due to its low surface charge and lower number of hydroxyl groups relative to bentonite and goethite. Carbazole showed the greatest interaction with goethite which would be expected for the ligand exchange mechanism as goethite has more hydroxyl groups available for interactions. Hexadecanol sorbed most to goethite followed by bentonite then kaolinite with the order predicted by the anion exchange capacity of these minerals (Ioannou et al., 2013, Mclaughlin et al., 1981, Schell and Jordan, 1959). These results suggest that the mechanism of sorption is similar or the same for the organic molecules on the three different minerals used in this study. If more widely applicable, this means that if the mechanism of interaction is known the interaction with different minerals may be predicted and vice versa.

Although, different minerals did promote different degrees of bonding within the different organic matter types the nature of the organic matter still seemed to be of greatest importance, with aromatic compounds showing the most sorption in all three minerals. Whilst studies in soils have found higher sorption in iron oxides than clay minerals (Mikutta et al., 2007), this was not observed in this study. As well as the more hydrophobic nature of the organic matter used in this study it is also important to consider the conditions of the experiment. In order to replicate marine conditions this experiment was carried out at pH 9, whereas soil-based experiments were conducted at pH 4. At pH 9, both iron oxides and clay minerals will be negatively charged, however whilst clays remain negatively charged at pH 4 iron oxides will become positively charged. Positively charged iron oxides are likely to be able to interact more favourably with organic matter that is predominantly negatively charged. This suggests that organic matter-iron oxide interactions in marine sediments may bear more resemblance to organic matter-clay interactions than is seen in soils.

7.3 Applications in the natural environment

The work carried out in Chapter 6 was part of the LOCATE project which aims to: (1) quantify the fate of terrigeneous organic matter from soils to the ocean, with particular focus on estuaries and coastal waters; (2) quantify and understand the loss processes in estuarine environments; and (3) build a new model of terrigeneous organic matter cycling valid in marine and fresh waters, and use it to predict the future evolution of the land ocean carbon flux. This study fed into this by investigating the impact of mineral sorption on the transport of dissolved organic matter (DOM) from rivers to the ocean. It also enabled a comparison of work in previous chapters within a more natural setting, albeit in the absence of particulate matter.

In this chapter three sources of DOM were used: two terrigeneous and one autochthonous. Measurements were via dissolved organic carbon (DOC), meaning the chemical structure of binding organic matter was not determined. However, fluorescence spectrometry did illustrate that the three sources had different chemical compositions. Organic matter type was found to have the least effect on organic matter-mineral sorption. Two possible causes of this have been identified. Firstly, the organic matter-mineral ratio was relatively high which means that the organic matter is likely to be in excess. Secondly, the results of Chapter 3 demonstrated that when a number of different organic compounds are present, sorption is cooperative with a minimal difference between the different compounds. As the organic matter used in this study contained a variety of different compounds this could be occurring here. Given a much higher ratio was achieved in Chapter 3, this suggests the second explanation, as it has been shown that higher ratios can be achieved. It is likely that the lower ratio achieved in Chapter 6 is due to the presence of only dissolved organic matter, which likely contains a limited number of compounds and few with a high affinity for the mineral surface, such as aromatic compounds.

Mineral mass, mineral type and salinity were also found to affect sorption. Increased mineral mass and increased salinity were both shown to have greatest impact on binding with both leading to an increased surface area for organic matter interactions. Increased salinity reduces the double layer allowing more Van der Waals interactions and provides more cations for cation bridging. The lower organic matter-mineral ratio achieved and the importance of increased surface area suggests that the organic matter may be forming thinner layers on the mineral than in the experiments involving the use of standards. This is likely due to the dissolved nature of the organic matter. Where in Chapter 3 the organic matter was insoluble, and therefore it was entropically favourable for it to leave the dissolved phase and bind to the organic matter already bound to the mineral, this will be considerably less favourable where the organic matter is dissolved. Indeed, whilst natural organic matter appears to bind in “blobs” (Ransom et al., 1997), few studies have looked at the resulting complexes of organic matter-mineral binding experiments.

7.4 Implications and further work

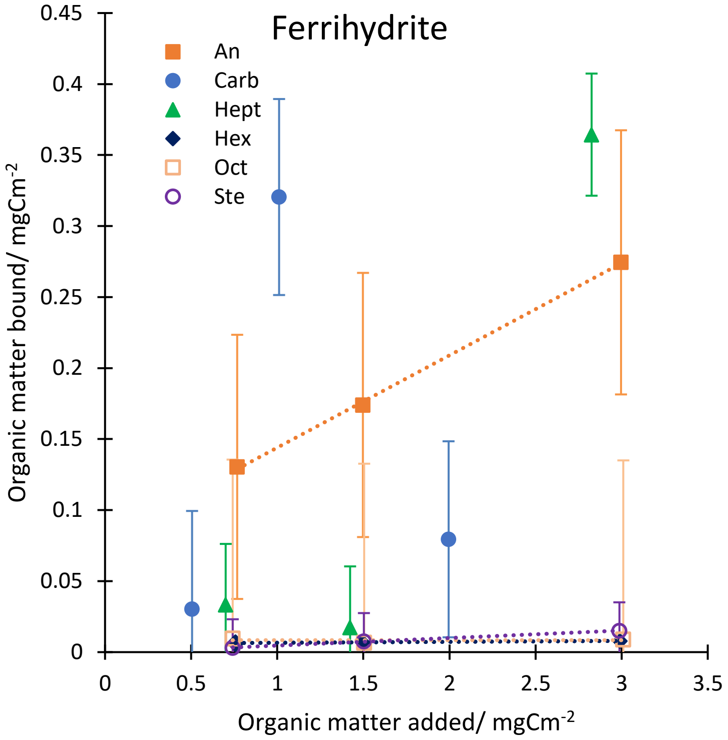
Organic matter-mineral interactions have been identified as important for the preservation of organic matter in marine sediments for a number of years. Consequently, many studies have been carried out in the area, however the complex nature of these interactions means there are still many questions unanswered. This work has demonstrated the importance of including particulate as well as dissolved organic matter in studies. In addition, it has been shown that organic matter can bind cooperatively, meaning that the presence of multiple types of organic matter may increase binding.

Further work is needed using a wider range of particulate organic matter including natural assemblages to see if the higher organic matter-mineral ratios achieved in this study are more widely applicable. Inclusion of particulate organic matter to mechanism studies would also be beneficial to determine the relative importance of the more hydrophobic interactions found here and the more specific ligand exchange and cation bridging found in dissolved organic matter studies. The methods developed in Chapter 2 should be able to facilitate such a study. This could also be used to investigate the interactions of natural organic matter with iron oxide minerals under marine conditions, to determine whether the similarity to clay mineral interaction is repeated with natural organic matter and wider selection of iron oxides.

The high organic matter-mineral ratios achieved in Chapter 3 raise further questions about the cause of the monolayer equivalent seen in marine sediments. Initially, experiments looking at the desorption and decomposition of these higher organic matter-mineral ratio complexes could be carried out to see how viable they are long term. Desorption could be carried out by isolating the bound clay by centrifugation and exposing it to fresh artificial seawater; this could be repeated a number of times to see if further desorption could be achieved. Decomposition experiments could also be carried out by adding bacteria to the reaction vessels and bubbling with air rather than nitrogen. It would also be interesting to investigate how the organic matter in this study binds to the mineral (e.g. using transition electron microscopy) in comparison to natural marine sediments and laboratory experiments focusing only on dissolved organic matter.

Appendix A Ferrihydrite experiments

In addition to kaolinite, bentonite and goethite mineral experiments were also carried out with ferrihydrite, chosen to represent uncrystallised iron hydroxides. Due to the high surface area of ferrihydrite, as well as adjusting organic matter concentrations the mineral mass was also reduced to 0.05g. Ferrihydrite results showed much lower sorption than the other three minerals. This is thought to be due to the reduced mass, which was added to accommodate the high surface area. In anthracene, lines of best fit suggest sorption of approximately one tenth of that of kaolinite, the same proportion as the reduction in mass. However, erratic results in the other compounds indicate that rather than mass and surface area, being important to organic-matter minerals interactions, this reduced mass was simply too low for the extraction process to work effectively.



Compound	Line of best fit	R^2 value
Anthracene	y = 0.065x + 0.079	$R^2 = 0.9992$
Carbazole	Non-linear response	
Heptadecane	Non-linear response	
Hexadecanol	y = 0.0007x + 0.0059	$R^2 = 0.5338$
Octadecanamide	Non-linear response	
Stearic acid	y = 0.0053x - 0.0006	$R^2 = 0.9992$

Figure A.1. Sorption of different compounds to ferrihydrite.

Appendix B Chapter 6 dataset and tukey tests

B.1 Dataset

Data set used in the plots and statistical analysis in chapter 6

Organic matter	**Mineral**	**Mass/ mg**	**Salinity**	**Repeat**	**Start_DOC_ mgCpL**	**Control_DOC _mgCpL**	**End_DOC_ mgCpL**	**Percentage DOC sorbed**
A	B	20	R	1	17.16667	16.66667	18.3	-9.8
A	B	40	R	1	17.16667	16.66667	16	4
A	B	80	R	1	13.15	12.3	9.27	24.63415
A	B	20	S	1	8.493333	8.83	6.83	22.65006
A	B	40	S	1	16.76667	18.26667	18.2	0.364964
A	B	80	S	1	9.66	8.83	7.17	18.79955
B	B	20	R	1	16.43333	15.95	17.56	-10.094
B	B	40	R	1	16.43333	15.95	15.2	4.702194
B	B	80	R	1	16.43333	15.95	15	5.956113
B	B	20	S	1	16.83333	15.86667	14	11.76471
B	B	40	S	1	16.83333	15.86667	14.1	11.13445
B	B	80	S	1	16.83333	15.86667	13.6	14.28571
C	B	20	R	1	13.53333	11.1	12.4	-11.7117
C	B	40	R	1	13.53333	11.1	10.9	1.801802
C	B	80	R	1	13.53333	11.1	11.8	-6.30631
C	B	20	S	1	12.6	10.9	9.14	16.14679
C	B	40	S	1	12.6	10.9	8.06	26.05505
C	B	80	S	1	12.6	10.9	7.73	29.08257
A	B	20	R	2	13.15	12.3	12.3	0
A	B	40	R	2	13.15	12.3	11.7	4.878049
A	B	80	R	2	13.15	12.3	13	-5.69106
A	B	20	S	2	13.73333	12.1	11	9.090909
A	B	40	S	2	13.73333	12.1	11	9.090909
A	B	80	S	2	13.73333	12.1	9.17	24.21488
B	B	20	R	2	12.73333	12.03333	11.9	1.108033
B	B	40	R	2	12.73333	12.03333	10.9	9.418283
B	B	80	R	2	12.73333	12.03333	11	8.587258
B	B	20	S	2	13.6	12.36667	11.5	7.008086
B	B	40	S	2	13.6	12.36667	11	11.05121
B	B	80	S	2	13.6	12.36667	10.7	13.47709
C	B	20	R	2	5.573333	5.883333	5.05	14.16431
C	B	40	R	2	5.573333	5.883333	5.49	6.685552
C	B	80	R	2	5.573333	5.883333	5.71	2.946176
C	B	20	S	2	6.223333	6.083333	4.88	19.78082
C	B	40	S	2	6.223333	6.083333	5.51	9.424658

Appendix B

Organic matter	Mineral	Mass/ mg	Salinity	Repeat	Start_DOC_ mgCpL	Control_DOC _mgCpL	End_DOC_ mgCpL	Percentage DOC sorbed
C	B	80	S	2	6.223333	6.083333	4.42	27.34247
A	B	20	R	3	9.845	8.855	9.03	-1.97628
A	B	40	R	3	9.845	8.855	8.79	0.734049
A	B	80	R	3	9.845	8.855	9.41	-6.26765
A	B	20	S	3	9.66	8.83	9.09	-2.94451
A	B	40	S	3	9.66	8.83	8.03	9.060023
A	B	80	S	3	9.66	8.83	7.46	15.51529
B	B	20	R	3	12.56667	11.66667	11.2	4
B	B	40	R	3	12.56667	11.66667	10.6	9.142857
B	B	80	R	3	12.56667	11.66667	10.8	7.428571
B	B	20	S	3	13.5	12.45	12	3.614458
B	B	40	S	3	13.5	12.45	10.6	14.85944
B	B	80	S	3	13.5	12.45	10.2	18.07229
C	B	20	R	3	6.07	5.7	6	-5.26316
C	B	40	R	3	6.07	5.7	5.26	7.719298
C	B	80	R	3	6.07	5.7	5.32	6.666667
C	B	20	S	3	7.123333	6.85	6.7	2.189781
C	B	40	S	3	7.123333	6.85	5.47	20.14599
C	B	80	S	3	7.123333	6.85	4.89	28.61314
A	K	20	R	1	17.16667	16.66667	16.9	-1.4
A	K	40	R	1	17.16667	16.66667	14.6	12.4
A	K	80	R	1	13.15	12.3	11.7	4.878049
A	K	20	S	1	16.76667	18.26667	15.2	16.78832
A	K	40	S	1	16.76667	18.26667	17.1	6.386861
A	K	80	S	1	13.15	12.1	11.1	8.264463
B	K	20	R	1	16.43333	15.95	15.1	5.329154
B	K	40	R	1	16.43333	15.95	13	18.4953
B	K	80	R	1	16.43333	15.95	14.1	11.59875
B	K	20	S	1	16.83333	15.86667	14.8	6.722689
B	K	40	S	1	16.83333	15.86667	15	5.462185
B	K	80	S	1	16.83333	15.86667	14.5	8.613445
C	K	20	R	1	13.53333	11.1	12.1	-9.00901
C	K	40	R	1	13.53333	11.1	9.07	18.28829
C	K	80	R	1	13.53333	11.1	11	0.900901
C	K	20	S	1	12.6	10.9	12.6	-15.5963
C	K	40	S	1	12.6	10.9	10.5	3.669725
C	K	80	S	1	12.6	10.9	9.32	14.49541
A	K	20	R	2	13.15	12.3	13.1	-6.50407
A	K	40	R	2	13.15	12.3	11.4	7.317073
A	K	80	R	2	13.15	12.3	13.7	-11.3821
A	K	20	S	2	13.73333	12.1	11.6	4.132231
A	K	40	S	2	13.73333	12.1	11.3	6.61157
A	K	80	S	2	13.73333	12.1	11	9.090909

Organic matter	Mineral	Mass/mg	Salinity	Repeat	Start_DOC_mgCpL	Control_DOC_mgCpL	End_DOC_mgCpL	Percentage DOC sorbed
B	K	20	R	2	12.73333	12.03333	12.8	-6.37119
B	K	40	R	2	12.73333	12.03333	12.1	-0.55402
B	K	80	R	2	12.73333	12.03333	11.1	7.756233
B	K	20	S	2	13.5	12.45	11.7	6.024096
B	K	40	S	2	13.6	12.36667	11.6	6.199461
B	K	80	S	2	13.6	12.36667	11.9	3.773585
C	K	20	R	2	5.573333	5.883333	4.79	18.58357
C	K	40	R	2	5.573333	5.883333	5.17	12.12465
C	K	80	R	2	5.573333	5.883333	5.17	12.12465
C	K	20	S	2	6.223333	6.083333	5.58	8.273973
C	K	40	S	2	6.223333	6.083333	5.23	14.0274
C	K	80	S	2	6.223333	6.083333	5.21	14.35616
A	K	20	R	3	9.845	8.855	8.23	7.058159
A	K	40	R	3	9.845	8.855	8.79	0.734049
A	K	80	R	3	9.845	8.855	8.77	0.95991
A	K	20	S	3	9.66	8.83	8.6	2.604757
A	K	40	S	3	9.66	8.83	7.92	10.30578
A	K	80	S	3	9.66	8.83	7.82	11.43828
B	K	20	R	3	12.56667	11.66667	11.5	1.428571
B	K	40	R	3	12.56667	11.66667	11.3	3.142857
B	K	80	R	3	12.56667	11.66667	11	5.714286
B	K	20	S	3	13.5	12.45	12.4	0.401606
B	K	40	S	3	13.5	12.45	11.4	8.433735
B	K	80	S	3	13.5	12.45	11.6	6.827309
C	K	20	R	3	6.07	5.7	5.68	0.350877
C	K	40	R	3	6.07	5.7	5.56	2.45614
C	K	80	R	3	6.07	5.7	5.6	1.754386
C	K	20	S	3	7.123333	6.85	6.82	0.437956
C	K	40	S	3	7.123333	6.85	6.59	3.79562
C	K	80	S	3	7.123333	6.85	5.7	16.78832
A	S	20	R	1	17.16667	16.66667	16.8	-0.8
A	S	40	R	1	17.16667	16.66667	14.7	11.8
A	S	80	R	1	9.845	8.855	7.43	16.0926
A	S	20	S	1	16.76667	18.26667	16.4	10.21898
A	S	40	S	1	16.76667	18.26667	16.1	11.86131
A	S	80	S	1	9.66	8.83	5.96	32.50283
B	S	20	R	1	16.43333	15.95	15.4	3.448276
B	S	40	R	1	16.43333	15.95	14.1	11.59875
B	S	80	R	1	16.43333	15.95	14	12.22571
B	S	20	S	1	16.83333	15.86667	14.8	6.722689
B	S	40	S	1	16.83333	15.86667	14.5	8.613445
B	S	80	S	1	16.83333	15.86667	12.4	21.84874
C	S	20	R	1	13.53333	11.1	10.6	4.504505

Appendix B

Organic matter	Mineral	Mass/ mg	Salinity	Repeat	Start_DOC_ mgCpL	Control_DOC _mgCpL	End_DOC_ mgCpL	Percentage DOC sorbed
C	S	40	R	1	13.53333	11.1	10.6	4.504505
C	S	80	R	1	13.53333	11.1	9.18	17.2973
C	S	20	S	1	12.6	10.9	10.7	1.834862
C	S	40	S	1	12.6	10.9	9.65	11.46789
C	S	80	S	1	12.6	10.9	9.61	11.83486
A	S	20	R	2	13.15	12.3	12.1	1.626016
A	S	40	R	2	13.15	12.3	10.9	11.38211
A	S	80	R	2	13.15	12.3	9.32	24.22764
A	S	20	S	2	13.73333	12.1	10.7	11.57025
A	S	40	S	2	13.73333	12.1	10.5	13.22314
A	S	80	S	2	13.73333	12.1	9.19	24.04959
B	S	20	R	2	12.73333	12.03333	12.4	-3.04709
B	S	40	R	2	12.73333	12.03333	11.5	4.432133
B	S	80	R	2	12.73333	12.03333	10.3	14.40443
B	S	20	S	2	13.6	12.36667	11.1	10.24259
B	S	40	S	2	13.6	12.36667	11.6	6.199461
B	S	80	S	2	13.6	12.36667	10.5	15.09434
C	S	20	R	2	5.573333	5.883333	5.94	-0.96317
C	S	40	R	2	5.573333	5.883333	5.67	3.626062
C	S	80	R	2	5.573333	5.883333	5.36	8.895184
C	S	20	S	2	6.223333	6.083333	5.48	9.917808
C	S	40	S	2	6.223333	6.083333	5.39	11.39726
C	S	80	S	2	6.223333	6.083333	5.28	13.20548
A	S	20	R	3	9.845	8.855	8.11	8.413326
A	S	40	R	3	9.845	8.855	7.99	9.768492
A	S	80	R	3	9.845	8.855	7.28	17.78656
A	S	20	S	3	9.66	8.83	7.85	11.09853
A	S	40	S	3	9.66	8.83	7.32	17.10079
A	S	80	S	3	9.66	8.83	6.65	24.68856
B	S	20	R	3	12.56667	11.66667	12.3	-5.42857
B	S	40	R	3	12.56667	11.66667	10.9	6.571429
B	S	80	R	3	12.56667	11.66667	10.3	11.71429
B	S	20	S	3	13.5	12.45	12.1	2.811245
B	S	40	S	3	13.5	12.45	11.4	8.433735
B	S	80	S	3	13.5	12.45	10.7	14.05622
C	S	20	R	3	6.07	5.7	5.6	1.754386
C	S	40	R	3	6.07	5.7	5.46	4.210526
C	S	80	R	3	6.07	5.7	5.22	8.421053
C	S	20	S	3	7.123333	6.85	6.81	0.583942
C	S	40	S	3	7.123333	6.85	6.05	11.67883
C	S	80	S	3	7.123333	6.85	5.86	14.45255

B.2 Tukey tests

Tukey tests performed on the ANOVA data in chapter 6

	Difference	**P value**	**Significance**	**Lower Confidence Level**	**Upper Confidence Level**
Salinity					
Marine - Riverine	6.429941	0	***	4.452334	8.407547
Organic_matter					
Autochthonous - Terrigenous 1	-0.19848	0.9856		-3.10031	2.703356
Autochthonous - Terrigenous 2	1.06433	0.661		-1.83751	3.966166
Terrigenous 1 - Terrigenous 2	1.26281	0.5589		-1.63903	4.164645
Mineral					
Bangor soil - Bentonite	1.626342	0.3825		-1.27549	4.528177
Bangor soil - Kaolinite	4.419841	0.0012	**	1.518006	7.321677
Bentonite - Kaolinite	2.793499	0.0619	.	-0.10834	5.695335
Mass_mg					
20 - 40	-5.25821	1.00E-04	***	-8.16004	-2.35637
20 - 80	-8.78918	0	***	-11.691	-5.88734
40 - 80	-3.53097	0.0126	*	-6.43281	-0.62914
Salinity:Mineral					
Marine:Bangor soil - Riverine:Bentonite	9.972103	0	***	4.96703	14.97718
Marine:Bentonite - Riverine:Bentonite	11.94176	0	***	6.93669	16.94684
Marine:Bentonite - Riverine:Kaolinite	10.06353	0	***	5.058457	15.0686
Marine:Bangor soil - Riverine:Kaolinite	8.09387	1.00E-04	***	3.088796	13.09894
Marine:Bentonite - Marine:Kaolinite	7.465231	4.00E-04	***	2.460158	12.47031
Marine:Bentonite - Riverine:Bangor soil	6.719419	0.0022	**	1.714346	11.72449

	Difference	**P value**	**Significance**	**Lower Confidence Level**	**Upper Confidence Level**
Marine:Bangor soil - Marine:Kaolinite	5.495571	0.0224	*	0.490497	10.50064
Riverine:Bangor soil - Riverine:Bentonite	5.222344	0.0354	*	0.217271	10.22742
Marine:Bangor soil - Riverine:Bangor soil	4.749759	0.0735	.	-0.25531	9.754833
Marine:Kaolinite - Riverine:Bentonite	4.476532	0.1081		-0.52854	9.481606
Riverine:Bangor soil - Riverine:Kaolinite	3.344111	0.3885		-1.66096	8.349185
Marine:Kaolinite - Riverine:Kaolinite	2.598299	0.6654		-2.40677	7.603373
Marine:Bangor soil - Marine:Bentonite	-1.96966	0.8654		-6.97473	3.035413
Riverine:Bentonite - Riverine:Kaolinite	-1.87823	0.8872		-6.88331	3.126841
Marine:Kaolinite - Riverine:Bangor soil	-0.74581	0.9981		-5.75089	4.259262
Organic_matter:Mineral					
Terrigenous 1:Bangor soil - Terrigenous 1:Kaolinite	9.273695	8.00E-04	***	2.589934	15.95746
Terrigenous 1:Bangor soil - Terrigenous 2:Kaolinite	8.75626	0.002	**	2.072499	15.44002
Terrigenous 1:Bangor soil - Terrigenous 1:Bentonite	7.792079	0.0099	**	1.108318	14.47584
Autochthonous :Kaolinite - Terrigenous 1:Bangor soil	-7.71045	0.0113	*	-14.3942	-1.02669
Autochthonous :Bangor soil - Terrigenous 1:Bangor soil	-6.55483	0.0592	.	-13.2386	0.128933
Terrigenous 1:Bangor soil - Terrigenous 2:Bentonite	6.17189	0.0953	.	-0.51187	12.85565
Terrigenous 1:Bangor soil - Terrigenous 2:Bangor soil	5.926051	0.1268		-0.75771	12.60981

	Difference	**P value**	**Significance**	**Lower Confidence Level**	**Upper Confidence Level**
Autochthonous :Bentonite - Terrigenous 1:Kaolinite	5.877758	0.1338		-0.806	12.56152
Autochthonous :Bentonite - Terrigenous 2:Kaolinite	5.360324	0.2287		-1.32344	12.04408
Autochthonous :Bentonite - Terrigenous 1:Bentonite	4.396142	0.4971		-2.28762	11.0799
Autochthonous :Bentonite - Autochthonous :Kaolinite	4.314511	0.5235		-2.36925	10.99827
Autochthonous :Bentonite - Terrigenous 1:Bangor soil	-3.39594	0.8036		-10.0797	3.287825
Terrigenous 1:Kaolinite - Terrigenous 2:Bangor soil	-3.34764	0.8157		-10.0314	3.336117
Autochthonous :Bangor soil - Autochthonous :Bentonite	-3.15889	0.8594		-9.84265	3.52487
Terrigenous 1:Kaolinite - Terrigenous 2:Bentonite	-3.1018	0.8714		-9.78557	3.581956
Terrigenous 2:Bangor soil - Terrigenous 2:Kaolinite	2.830209	0.9197		-3.85355	9.51397
Autochthonous :Bentonite - Terrigenous 2:Bentonite	2.775954	0.9276		-3.90781	9.459715
Autochthonous :Bangor soil - Terrigenous 1:Kaolinite	2.718867	0.9354		-3.96489	9.402628
Terrigenous 2:Bentonite - Terrigenous 2:Kaolinite	2.58437	0.9515		-4.09939	9.268131
Autochthonous :Bentonite - Terrigenous 2:Bangor soil	2.530115	0.9571		-4.15365	9.213876

	Difference	P value	Significance	Lower Confidence Level	Upper Confidence Level
Autochthonous :Bangor soil - Terrigenous 2:Kaolinite	2.201433	0.9816		-4.48233	8.885194
Terrigenous 1:Bentonite - Terrigenous 2:Bangor soil	-1.86603	0.9937		-8.54979	4.817734
Autochthonous:Kaolinite - Terrigenous 2:Bangor soil	-1.7844	0.9954		-8.46816	4.899365
Terrigenous 1:Bentonite - Terrigenous 2:Bentonite	-1.62019	0.9976		-8.30395	5.063573
Autochthonous:Kaolinite - Terrigenous 1:Kaolinite	1.563248	0.9982		-5.12051	8.247009
Autochthonous:Kaolinite - Terrigenous 2:Bentonite	-1.53856	0.9984		-8.22232	5.145204
Terrigenous 1:Bentonite - Terrigenous 1:Kaolinite	1.481616	0.9988		-5.20214	8.165377
Autochthonous:Bangor soil - Terrigenous 1:Bentonite	1.237251	0.9997		-5.44651	7.921012
Autochthonous:Bangor soil - Autochthonous:Kaolinite	1.15562	0.9998		-5.52814	7.839381
Autochthonous:Kaolinite - Terrigenous 2:Kaolinite	1.045813	0.9999		-5.63795	7.729574
Terrigenous 1:Bentonite - Terrigenous 2:Kaolinite	0.964182	0.9999		-5.71958	7.647943
Autochthonous:Bangor soil - Terrigenous 2:Bangor soil	-0.62878	1		-7.31254	6.054985
Autochthonous:Bangor soil - Terrigenous 2:Bentonite	-0.38294	1		-7.0667	6.300823
Autochthonous:Kaolinite - Terrigenous 1:Bentonite	0.081631	1		-6.60213	6.765392

	Difference	**P value**	**Significance**	**Lower Confidence Level**	**Upper Confidence Level**
Terrigenous 1:Kaolinite - Terrigenous 2:Kaolinite	-0.51743	1		-7.2012	6.166326
Terrigenous 2:Bangor soil - Terrigenous 2:Bentonite	0.245839	1		-6.43792	6.9296
Mineral:Mass_mg					
Bangor soil:20 - Bangor soil:80	-12.6827	0	***	-19.3665	-5.99898
Bangor soil:80 - Bentonite:20	12.94832	0	***	6.264556	19.63208
Bangor soil:80 - Kaolinite:20	14.64125	0	***	7.957493	21.32502
Bentonite:80 - Kaolinite:20	10.45009	1.00E-04	***	3.766324	17.13385
Bangor soil:80 - Kaolinite:80	9.713612	3.00E-04	***	3.029851	16.39737
Bangor soil:80 - Kaolinite:40	9.083404	0.0011	**	2.399643	15.76717
Bentonite:20 - Bentonite:80	-8.75715	0.002	**	-15.4409	-2.07339
Bangor soil:20 - Bentonite:80	-8.49157	0.0031	**	-15.1753	-1.80781
Bangor soil:80 - Bentonite:40	7.918287	0.0081	**	1.234526	14.60205
Bangor soil:40 - Bangor soil:80	-7.496	0.0157	*	-14.1798	-0.81224
Bangor soil:40 - Kaolinite:20	7.145251	0.0264	*	0.46149	13.82901
Bentonite:40 - Kaolinite:20	6.722967	0.0475	*	0.039206	13.40673
Kaolinite:20 - Kaolinite:40	-5.55785	0.1882		-12.2416	1.125911
Bentonite:80 - Kaolinite:80	5.522443	0.195		-1.16132	12.2062
Bangor soil:40 - Bentonite:20	5.452313	0.2092		-1.23145	12.13607
Bangor soil:20 - Bangor soil:40	-5.18674	0.2689		-11.8705	1.497021
Bentonite:20 - Bentonite:40	-5.03003	0.3087		-11.7138	1.653732

	Difference	P value	Significance	Lower Confidence Level	Upper Confidence Level
Kaolinite:20 - Kaolinite:80	-4.92764	0.3364		-11.6114	1.756119
Bentonite:80 - Kaolinite:40	4.892235	0.3462		-1.79153	11.576
Bangor soil:20 - Bentonite:40	-4.76446	0.383		-11.4482	1.919305
Bangor soil:80 - Bentonite:80	4.191169	0.5636		-2.49259	10.87493
Bentonite:20 - Kaolinite:40	-3.86491	0.6685		-10.5487	2.818849
Bentonite:40 - Bentonite:80	-3.72712	0.7108		-10.4109	2.956643
Bangor soil:20 - Kaolinite:40	-3.59934	0.7483		-10.2831	3.084422
Bangor soil:40 - Bentonite:80	-3.30483	0.8262		-9.9886	3.378926
Bentonite:20 - Kaolinite:80	-3.2347	0.8427		-9.91847	3.449056
Bangor soil:20 - Kaolinite:80	-2.96913	0.8967		-9.65289	3.714629
Bangor soil:40 - Kaolinite:80	2.217608	0.9807		-4.46615	8.901369
Bangor soil:20 - Kaolinite:20	1.958511	0.9914		-4.72525	8.642272
Bentonite:40 - Kaolinite:80	1.795325	0.9952		-4.88844	8.479086
Bentonite:20 - Kaolinite:20	1.692938	0.9968		-4.99082	8.376699
Bangor soil:40 - Kaolinite:40	1.587401	0.998		-5.09636	8.271162
Bentonite:40 - Kaolinite:40	1.165117	0.9998		-5.51864	7.848878
Bangor soil:20 - Bentonite:20	0.265573	1		-6.41819	6.949334
Bangor soil:40 - Bentonite:40	0.422284	1		-6.26148	7.106045
Kaolinite:40 - Kaolinite:80	0.630207	1		-6.05355	7.313969

Glossary of Terms

Absorption	Interaction with a solid at the surface and interior
Adsorption	Interaction with a solid at the surface only
Carbon cycle	The movement of carbon through the surface, interior and atmosphere of the Earth
Chelate effect	Stronger interaction of a ligand able to bond to a metal centre via multiple bonds
Clay	Aluminium silicate with layered structure
Clay size fraction	Particles less than 4µm in size
Desorption	Removal from a solid
Dissolved organic matter (DOM)	That able to pass through a GF/F filter in Marine science and a GF/C filter in soil science
Enthalpy	Heat content per unit mass of a substance measured as the internal energy plus the product of its pressure and volume
Entropy	Measure of the disorder in a thermodynamic system
Equimolar	The same number of moles of each was added
Hydrophilic	Water loving/ fat hating
Hydrophobic	Water hating/fat loving
Labile organic matter	Organic matter more susceptible to degradation
Monolayer equivalent	Organic matter: mineral ratio equivalent to monolayer coverage
Monolayer hypothesis	Hypothesis that organic matter is preserved as a thin uniform layer across the mineral surface
Particulate organic matter (POM)	That unable to pass through a GF/F filter in Marine science and a GF/C filter in soil science
pKa	Negative log of the acid dissociation constant Ka. Giving an indication of the strength of the acid
pKb	Negative log of the base dissociation constant Kb. Giving an indication of the strength of the base
Point of zero charge	pH at which the net charge of a mineral surface is zero
Sorption	Covers both absorption and adsorption

Bibliography

ABOMOHRA, A., EL-SHEEKH, M. & HANELT, D. 2017. Screening of marine microalgae isolated from the hypersaline Bardawil lagoon for biodiesel feedstock. *Renewable Energy,* 101**,** 1266-1272.

AHMAT, A. M., BOUSSAFIR, M., LE MILBEAU, C., GUEGAN, R., VALDES, J., GUINEZ, M., SIFEDDINE, A. & LE FORESTIER, L. 2015. Organic matter-clay interaction along a seawater column of the Eastern Pacific upwelling system (Antofagasta bay, Chile): Implications for source rock organic matter preservation. *Marine Chemistry,* 179**,** 23-33.

AHMAT, A. M., BOUSSAFIR, M., LE MILBEAU, C., GUEGAN, R., VALDES, J., GUINEZ, M., SIFEDDINE, A. & LE FORESTIER, L. 2016. Organic matter-clay interaction along a seawater column of the Eastern Pacific upwelling system (Antofagasta bay, Chile): Implications for source rock organic matter preservation. *Marine Chemistry,* 179**,** 23-33.

ALLABY, M. 2008. *Dictionary of Earth Sciences*, Oxford University Press.

ANDERSON, T. R., ROWE, E. C., POLIMENE, L., TIPPING, E., EVANS, C. D., BARRY, C. D. G., HANSELL, D. A., KAISER, K., KITIDIS, V., LAPWORTH, D. J., MAYOR, D. J., MONTEITH, D. T., PICKARD, A. E., SANDERS, R. J., SPEARS, B. M., TORRES, R., TYE, A. M., WADE, A. J. & WASKA, H. 2019. Unified concepts for understanding and modelling turnover of dissolved organic matter from freshwaters to the ocean: the UniDOM model. *Biogeochemistry*.

ARCHER, D. 2010. The Global Carbon Cycle. *The Global Carbon Cycle by David Archer. Princeton University Press, 1996. ISBN: 978-0-691-14414-6*.

ARNARSON, T. S. & KEIL, R. G. 2000. Mechanisms of pore water organic matter adsorption to montmorillonite. *Marine Chemistry,* 71**,** 309-320.

ARNARSON, T. S. & KEIL, R. G. 2001. Organic-mineral interactions in marine sediments studied using density fractionation and X-ray photoelectron spectroscopy. *Organic Geochemistry,* 32**,** 1401-1415.

ARNARSON, T. S. & KEIL, R. G. 2005. Influence of organic-mineral aggregates on microbial degradation of the dinoflagellate Scrippsiella trochoidea. *Geochimica Et Cosmochimica Acta,* 69**,** 2111-2117.

AUFDENKAMPE, A. K., HEDGES, J. I., RICHEY, J. E., KRUSCHE, A. V. & LLERENA, C. A. 2001. Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin. *Limnology and Oceanography,* 46**,** 1921-1935.

AVNERI-KATZ, S., YOUNG, R. B., MCKENNA, A. M., CHEN, H., CORILO, Y. E., POLUBESOVA, T., BORCH, T. & CHEFETZ, B. 2017. Adsorptive fractionation of dissolved organic matter (DOM) by mineral soil: Macroscale approach and molecular insight. *Organic Geochemistry,* 103**,** 113-124.

BAIK, M. H. & LEE, S. Y. 2010. Colloidal stability of bentonite clay considering surface charge properties as a function of pH and ionic strength. *Journal of Industrial and Engineering Chemistry,* 16**,** 837-841.

BARBER, A., LALONDE, K., MUCCI, A. & GELINAS, Y. 2014. The role of iron in the diagenesis of organic carbon and nitrogen in sediments: A long-term incubation experiment. *Marine Chemistry,* 162**,** 1-9.

BOCK, M. J. & MAYER, L. M. 2000. Mesodensity organo-clay associations in a near-shore sediment. *Marine Geology,* 163**,** 65-75.

BOUDOT, J. P., BRAHIM, A. B. H., STEIMAN, R. & SEIGLEMURANDI, F. 1989. Biodegradation of synthetic organo-metallic complexes of iron and aluminum with selected metal to carbon ratios. *Soil Biology & Biochemistry,* 21**,** 961-966.

BRO, R. 1997. PARAFAC. Tutorial and applications. *Chemometrics and intelligent laboratory systems,* 38**,** 149-171.

CARTAPANIS, O., BIANCHI, D., JACCARD, S. L. & GALBRAITH, E. D. 2016. Global pulses of organic carbon burial in deep-sea sediments during glacial maxima. *Nature Communications,* 7**,** 7.

CARTER, P. W. 1978. Adsorption of amino acid-containing organic-matter by calcite and quartz. *Geochimica Et Cosmochimica Acta,* 42**,** 1239-1242.

CHEN, W., WESTERHOFF, P., LEENHEER, J. A. & BOOKSH, K. 2003. Fluorescence excitation - Emission matrix regional integration to quantify spectra for dissolved organic matter. *Environmental Science & Technology,* 37**,** 5701-5710.

CHIPERA, S. J. & BISH, D. L. 2002. FULLPAT: a full-pattern quantitative analysis program for X-ray powder diffraction using measured and calculated patterns. *Journal of Applied Crystallography,* 35**,** 744-749.

CIAIS, P., SABINE, C., BALA, G., BOPP, L., BROVKIN, V., CANADELL, J., CHHABRA, A., DEFRIES, R., GALLOWAY, J., HEIMANN, M., JONES, C., LE QUÉRÉ, C., MYNENI, R. B., PIAO, S. & THORNTON, P. 2013. *Carbon and Other Biogeochemical Cycles. In: climate change 2013: the physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change*, [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

COBLE, P. G. 1996. Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy. *Marine Chemistry,* 51**,** 325-346.

CORNELL, R. M. & SCHWERTMANN, U. 2003. *The iron Oxides Structure, Properties, Reactions, Occurrences and Uses*, Wiley-VCH.

CURRY, K. J., BENNETT, R. H., MAYER, L. M., CURRY, A., ABRIL, M., BIESIOT, P. M. & HULBERT, M. H. 2007. Direct visualization of clay microfabric signatures driving organic matter preservation in fine-grained sediment. *Geochimica Et Cosmochimica Acta,* 71**,** 1709-1720.

DAVIS, J. A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochimica et Cosmochimica Acta,* 46**,** 2381-2393.

DELLE SITE, A. 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *Journal of Physical and Chemical Reference Data,* 30**,** 187-439.

DING, C. L. & SHANG, C. I. 2010. Mechanisms controlling adsorption of natural organic matter on surfactant-modified iron oxide-coated sand. *Water Research,* 44**,** 3651-3658.

DING, X. L. & HENRICHS, S. M. 2002. Adsorption and desorption of proteins and polyamino acids by clay minerals and marine sediments. *Marine Chemistry,* 77**,** 225-237.

DROUIN, S., BOUSSAFIR, M., ROBERT, J. L., ALBERIC, P. & DURAND, A. 2010. Carboxylic acid sorption on synthetic clays in sea water: In vitro experiments and implications for organo-clay behaviour under marine conditions. *Organic Geochemistry,* 41**,** 192-199.

DUMIG, A., HAUSLER, W., STEFFENS, M. & KOGEL-KNABNER, I. 2012. Clay fractions from a soil chronosequence after glacier retreat reveal the initial evolution of organo-mineral associations. *Geochimica Et Cosmochimica Acta,* 85**,** 1-18.

EBERL, D. D. 2003. *User's guide to RockJock – A program for determining quantitative mineralogy from powder X-ray diffraction data DATA.,* Open-File Report 03-78, U.S. Geological Survey.

FENG, X. J., SIMPSON, A. J. & SIMPSON, M. J. 2005. Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces. *Organic Geochemistry,* 36**,** 1553-1566.

FRIEDLINGSTEIN, P. 2015. Carbon cycle feedbacks and future climate change. *Philosophical transactions. Series A, Mathematical, physical, and engineering sciences,* 373.

GREENLAND, D. J. 1971. Interactions between humic and fulvic acids and clays. *Soil Science,* 111**,** 34-41.

GU, B., SCHMITT, J., CHEN, Z., LIANG, L. & MCCARTHY, J. F. 1995. Adsorption and desorption of different organic matter fractions on iron oxide. *Geochimica et Cosmochimica Acta,* 59**,** 219-229.

GUIRY, W. 1996. *AlgaeBase* [Online]. National Univeristy of Ireland: World-wide electronic publication. [Accessed 03.03 2017].

HEDGES, J. I., BALDOCK, J. A., GELINAS, Y., LEE, C., PETERSON, M. & WAKEHAM, S. G. 2001. Evidence for non-selective preservation of organic matter in sinking marine particles. *Nature,* 409**,** 801-804.

HEDGES, J. I., CLARK, W. A. & COWIE, G. L. 1988. Fluxes and reactivities of organic-matter in a coastal marine bay. *Limnology and Oceanography,* 33**,** 1137-1152.

HEDGES, J. I. & KEIL, R. G. 1995. Sedimentary organic-matter preservation - an assessment and speculative synthesis. *Marine Chemistry,* 49**,** 81-115.

HEIL, D. & SPOSITO, G. 1993. Organic-matter role in illitic soil colloids flocculation .1. Counter ions and ph. *Soil Science Society of America Journal,* 57**,** 1241-1246.

HEINZE, C., EYRING, V., FRIEDLINGSTEIN, P., JONES, C., BALKANSKI, Y., COLLINS, W., FICHEFET, T., GAO, S., HALL, A., IVANOVA, D., KNORR, W., KNUTTI, R., LOEW, A., PONATER, M., SCHULTZ, M. G., SCHULZ, M., SIEBESMA, P., TEIXEIRA, J., TSELIOUDIS, G. & VANCOPPENOLLE, M. 2019. ESD Reviews: Climate feedbacks in the Earth system and prospects for their evaluation. *Earth System Dynamics,* 10**,** 379-452.

HENRICHS, S. M. 1995. Sedimentary organic-matter preservation - an assessment and speculative synthesis - a comment. *Marine Chemistry,* 49**,** 127-136.

HENRICHS, S. M. & SUGAI, S. F. 1993. Adsorption of amino-acids and glucose by sediments of resurrection bay, alaska, USA - functional-group effects. *Geochimica Et Cosmochimica Acta,* 57**,** 823-835.

IOANNOU, Z., DIMIRKOU, A. & IOANNOU, A. 2013. Phosphate Adsorption from Aqueous Solutions onto Goethite, Bentonite, and Bentonite–Goethite System. *Water, Air, & Soil Pollution,* 224**,** 1374.

JIN, J. & ZIMMERMAN, A. R. 2010. Abiotic interactions of natural dissolved organic matter and carbonate aquifer rock. *Applied Geochemistry,* 25**,** 472-484.

KAISER, K. & GUGGENBERGER, G. 2000. The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Organic Geochemistry,* 31**,** 711-725.

KANG, S. H. & XING, B. S. 2005. Phenanthrene sorption to sequentially extracted soil humic acids and humins. *Environmental Science & Technology,* 39**,** 134-140.

KANG, S. H. & XING, B. S. 2008. Humic acid fractionation upon sequential adsorption onto goethite. *Langmuir,* 24**,** 2525-2531.

KEELING, C. D., BACASTOW, R. B., BAINBRIDGE, A. E., EKDAHL, C. A., GUENTHER, P. R., WATERMAN, L. S. & CHIN, J. F. S. 1976. Atmospheric carbon-dioxide variations at mauna-loa observatory, hawaii. *Tellus,* 28**,** 538-551.

KEIL, R. G. & HEDGES, J. I. 1993. Sorption of organic-matter to mineral surfaces and the preservation of organic-matter in coastal marine-sediments. *Chemical Geology,* 107**,** 385-388.

KEIL, R. G. & KIRCHMAN, D. L. 1994. Abiotic transformation of labile protein to refractory protein in sea-water. *Marine Chemistry,* 45**,** 187-196.

KEIL, R. G. & MAYER, L. M. 2014. *Mineral matrices and organic matter*, Elsevier.

KENNEDY, M. J., PEVEAR, D. R. & HILL, R. J. 2002. Mineral Surface Control of Organic Carbon in Black Shale. *Science,* 295**,** 657-660.

KENNEDY, M. J. & WAGNER, T. 2011. Clay mineral continental amplifier for marine carbon sequestration in a greenhouse ocean. *Proceedings of the National Academy of Sciences of the United States of America,* 108**,** 9776-9781.

KOMADA, T. & REIMERS, C. E. 2001. Resuspension-induced partitioning of organic carbon between solid and solution phases from a river-ocean transition. *Marine Chemistry,* 76**,** 155-174.

LALONDE, K., MUCCI, A., OUELLET, A. & GELINAS, Y. 2012. Preservation of organic matter in sediments promoted by iron. *Nature,* 483**,** 198-200.

LAPWORTH, D. J., GOODDY, D. C., BUTCHER, A. S. & MORRIS, B. L. 2008. Tracing groundwater flow and sources of organic carbon in sandstone aquifers using fluorescence properties of dissolved organic matter (DOM). *Applied Geochemistry,* 23**,** 3384-3390.

LAPWORTH, D. J. & KINNIBURGH, D. G. 2009. An R script for visualising and analysing fluorescence excitation-emission matrices (EEMs). *Computers & Geosciences,* 35**,** 2160-2163.

LE MOIGNE, F. A. C., GALLINARI, M., LAURENCEAU, E. & DE LA ROCHA, C. L. 2013. Enhanced rates of particulate organic matter remineralization by microzooplankton are diminished by added ballast minerals. *Biogeosciences,* 10**,** 5755-5765.

LEE, C., PETERSON, M. L., WAKEHAM, S. G., ARMSTRONG, R. A., COCHRAN, J. K., MIQUEL, J. C., FOWLER, S. W., HIRSCHBERG, D., BECK, A. & XUE, J. H. 2009. Particulate organic matter and ballast fluxes measured using time-series and settling velocity sediment traps in the northwestern Mediterranean Sea. *Deep-Sea Research Part Ii-Topical Studies in Oceanography,* 56**,** 1420-1436.

LI, M. X., PENG, C. H., WANG, M., XUE, W., ZHANG, K. R., WANG, K. F., SHI, G. H. & ZHU, Q. A. 2017. The carbon flux of global rivers: A re-evaluation of amount and spatial patterns. *Ecological Indicators,* 80**,** 40-51.

LIU, Z. F. & LEE, C. 2006. Drying effects on sorption capacity of coastal sediment: The importance of architecture and polarity of organic matter. *Geochimica Et Cosmochimica Acta,* 70**,** 3313-3324.

LU, D. W., SONG, Q. & WANG, X. C. 2010. Decomposition of algal lipids in clay-enriched marine sediment under oxic and anoxic conditions. *Chinese Journal of Oceanology and Limnology,* 28**,** 131-143.

MACKENZIE, F. T., LERMAN, A. & ANDERSSON, A. J. 2004. Past and present of sediment and carbon biogeochemical cycling models. *Biogeosciences,* 1**,** 11-32.

MAYER, L. M. 1994a. Relationships between mineral surfaces and organic-carbon concentrations in soils and sediments. *Chemical Geology,* 114**,** 347-363.

MAYER, L. M. 1994b. Surface-area control of organic-carbon accumulation in continental-shelf sediments. *Geochimica Et Cosmochimica Acta,* 58**,** 1271-1284.

MAYER, L. M. 1999. Extent of coverage of mineral surfaces by organic matter in marine sediments. *Geochimica Et Cosmochimica Acta,* 63**,** 207-215.

MAYER, L. M. 2004. The inertness of being organic. *Marine Chemistry,* 92**,** 135-140.

MAYER, L. M., MACKO, S. A. & CAMMEN, L. 1988. Provenance, concentrations and nature of sedimentary organic nitrogen in the gulf of maine. *Marine Chemistry,* 25**,** 291-304.

MAYER, L. M., RAHAIM, P. T., GUERIN, W., MACKO, S. A., WATLING, L. & ANDERSON, F. E. 1985. Biological and granulometric controls on sedimentary organic-matter of an intertidal mudflat. *Estuarine Coastal and Shelf Science,* 20**,** 491-503.

MCKNIGHT, D. M., BOYER, E. W., WESTERHOFF, P. K., DORAN, P. T., KULBE, T. & ANDERSEN, D. T. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography,* 46**,** 38-48.

MCLAUGHLIN, J. R., RYDEN, J. C. & SYERS, J. K. 1981. Sorption of inorganic phosphate by iron- and aluminium- containing components. *Journal of Soil Science,* 32**,** 365-378.

MEIER, M., NAMJESNIK-DEJANOVIC, K., MAURICE, P. A., CHIN, Y. P. & AIKEN, G. R. 1999. Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite. *Chemical Geology,* 157**,** 275-284.

MEYERS, P. A. & QUINN, J. G. 1973. Factors affecting association of fatty-acids with mineral particles in sea-water. *Geochimica Et Cosmochimica Acta,* 37**,** 1745-1759.

MEYERSSCHULTE, K. J. & HEDGES, J. I. 1986. Molecular evidence for a terrestrial component of organic-matter dissolved in ocean water. *Nature,* 321**,** 61-63.

MIKUTTA, R., MIKUTTA, C., KALBITZ, K., SCHEEL, T., KAISER, K. & JAHN, R. 2007. Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochimica Et Cosmochimica Acta,* 71**,** 2569-2590.

MURPHY, K. R., STEDMON, C. A., GRAEBER, D. & BRO, R. 2013. Fluorescence spectroscopy and multi-way techniques. PARAFAC. *Analytical Methods,* 5**,** 6557-6566.

NEWCOMB, C. J., QAFOKU, N. P., GRATE, J. W., BAILEY, V. L. & DE YOREO, J. J. 2017. Developing a molecular picture of soil organic matter-mineral interactions by quantifying organo-mineral binding (vol 8, 396, 2017). *Nature Communications,* 8**,** 1.

NEWMAN, A. C. D. 1987. *Chemistry of Clays and Clay Minerals*, Longman Scientific and Technical.

PACTON, M., FIET, N. & GORIN, G. E. 2007. Bacterial activity and preservation of sedimentary organic matter: The role of exopolymeric substances. *Geomicrobiology Journal,* 24**,** 571-581.

PEACOCK, M., FREEMAN, C., GAUCI, V., LEBRON, I. & EVANS, C. D. 2015. Investigations of freezing and cold storage for the analysis of peatland dissolved organic carbon (DOC) and absorbance properties. *Environmental Science-Processes & Impacts,* 17**,** 1290-1301.

PORRENGA, D. H. 1967. *Clay mineralogy and geochemistry of recent marine sediments in tropical areas: as exemplified by the Niger Delta, the Orinoco shelf and the shelf off Sarawak*, Stolk.

PRESTON, M. R. & RILEY, J. P. 1982. The interactions of humic compounds with electrolytes and three clay minerals under simulated estuarine conditions. *Estuarine, Coastal and Shelf Science,* 14**,** 567-576.

R-TEAM 2008. The R Foundation for Statistical Computing. Vienna, Austria: Vienna University of Technology.

RANSOM, B., BENNETT, R. H., BAERWALD, R. & SHEA, K. 1997. TEM study of in situ organic matter on continental margins: Occurrence and the ''monolayer'' hypothesis. *Marine Geology,* 138**,** 1-9.

RANSOM, B., KIM, D., KASTNER, M. & WAINWRIGHT, S. 1998. Organic matter preservation on continental slopes: Importance of mineralogy and surface area. *Geochimica Et Cosmochimica Acta,* 62**,** 1329-1345.

RASHID, M. A., BUCKLEY, D. E. & ROBERTSON, K. R. 1972. Interactions of a marine humic acid with clay minerals and a natural sediment. *Geoderma,* 8**,** 11-27.

SAIDY, A. R., SMERNIK, R. J., BALDOCK, J. A., KAISER, K. & SANDERMAN, J. 2013. The sorption of organic carbon onto differing clay minerals in the presence and absence of hydrous iron oxide. *Geoderma,* 209**,** 15-21.

SAIDY, A. R., SMERNIK, R. J., BALDOCK, J. A., KAISER, K. & SANDERMAN, J. 2015. Microbial degradation of organic carbon sorbed to phyllosilicate clays with and without hydrous iron oxide coating. *European Journal of Soil Science,* 66**,** 83-94.

SATTERBERG, J., ARNARSON, T. S., LESSARD, E. J. & KEIL, R. G. 2003. Sorption of organic matter from four phytoplankton species to montmorillonite, chlorite and kaolinite in seawater. *Marine Chemistry,* 81**,** 11-18.

SCHELL, W. R. & JORDAN, J. V. 1959. Anion-exchange studies of pure clays. *Plant and Soil,* 10**,** 303-318.

SCHMIDT, M. W. I., TORN, M. S., ABIVEN, S., DITTMAR, T., GUGGENBERGER, G., JANSSENS, I. A., KLEBER, M., KOGEL-KNABNER, I., LEHMANN, J., MANNING, D. A. C., NANNIPIERI, P.,

RASSE, D. P., WEINER, S. & TRUMBORE, S. E. 2011. Persistence of soil organic matter as an ecosystem property. *Nature,* 478**,** 49-56.

SCHNECKENBURGER, T., RIEFSTAHL, J. & FISCHER, K. 2018. Adsorption of aliphatic polyhydroxy carboxylic acids on gibbsite: pH dependency and importance of adsorbate structure. *Environmental Sciences Europe,* 30**,** 15.

SHAKER, A. M., KOMY, Z. R., HEGGY, S. E. M. & EL-SAYED, M. E. A. 2012. Kinetic Study for Adsorption Humic Acid on Soil Minerals. *Journal of Physical Chemistry A,* 116**,** 10889-10896.

SHOLKOVITZ, E. R. 1976. Flocculation of dissolved organic and inorganic matter during mixing of river water and seawater. *Geochimica Et Cosmochimica Acta,* 40**,** 831-845.

SONG, K. & SANDÍ, G. 2001. Characterization of Montmorillonite Surfaces After Modification by Organosilane. *Clays and Clay Minerals,* 49**,** 119-125.

SOTO-LEON, S., ZAZUETA-PATRON, I. E., PINA-VALDEZ, P., NIEVES-SOTO, M., REYES-MORENO, C. & CONTRERAS-ANDRADE, I. 2014. Tetraselmis suecica lipid extraction: Ultrasonic and solvent aided process. *Revista Mexicana De Ingenieria Quimica,* 13**,** 723-737.

STEDMON, C. A. & BRO, R. 2008. Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. *Limnology and Oceanography-Methods,* 6**,** 572-579.

STEDMON, C. A., MARKAGER, S. & BRO, R. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry,* 82**,** 239-254.

SUBOV, N. 1931. Oceanographical tables USSR Ocean. *Int. Hydrometeorol., Comm, Moscow*.

SWENSON, T. L., BOWEN, B. P., NICO, P. S. & NORTHEN, T. R. 2015. Competitive sorption of microbial metabolites on an iron oxide mineral. *Soil Biology & Biochemistry,* 90**,** 34-41.

TANOUE, E. & HANDA, N. 1979. Differential sorption of organic matter by various sized sediment particles in recent sediment from the bering sea. *Journal of the Oceanographical Society of Japan,* 35**,** 199-208.

TIPPING, E. 1981. The adsorption of aquatic humic substances by iron-oxides. *Geochimica Et Cosmochimica Acta,* 45**,** 191-199.

TSCHAPEK, M., TCHEICHVILI, L. & WASOWSKI, C. 1974. The point of zero charge (pzc) of kaolinite and SiO2+Al2O3 mixtures. *Clay Minerals,* 10**,** 219-229.

WANG, C., LI, F. C., SHI, H. Z., JIN, Z. D., SUN, X. H., ZHANG, F., WU, F. & KAN, S. 2013. The significant role of inorganic matters in preservation and stability of soil organic carbon in the Baoji and Luochuan loess/paleosol profiles, Central China. *Catena,* 109**,** 186-194.

WANG, K. J. & XING, B. S. 2005. Structural and sorption characteristics of adsorbed humic acid on clay minerals. *Journal of Environmental Quality,* 34**,** 342-349.

WANG, X. C. & LEE, C. 1993. Adsorption and desorption of aliphatic-amines, amino-acids and acetate by clay-minerals and marine-sediments. *Marine Chemistry,* 44**,** 1-23.

WEILER, R. R. & MILLS, A. A. 1965. Surface properties and pore structure of marine sediments. *Deep Sea Res,* 12**,** 511-529.

WISEMAN, C. L. S. & PUTTMANN, W. 2006. Interactions between mineral phases in the preservation of soil organic matter. *Geoderma,* 134**,** 109-118.

YEASMIN, S., SINGH, B., KOOKANA, R. S., FARRELL, M., SPARKS, D. L. & JOHNSTON, C. T. 2014. Influence of mineral characteristics on the retention of low molecular weight organic compounds: A batch sorption-desorption and ATR-FTIR study. *Journal of Colloid and Interface Science,* 432**,** 246-257.

ZADAKA, D., RADIAN, A. & MISHAEL, Y. G. 2010. Applying zeta potential measurements to characterize the adsorption on montmorillonite of organic cations as monomers, micelles, or polymers. *Journal of Colloid and Interface Science,* 352**,** 171-177.

ZHANG, J. C., ZHANG, L., WANG, P., HUANG, Q. W., YU, G. H., LI, D. C., SHEN, Q. R. & RAN, W. 2013. The role of non-crystalline Fe in the increase of SOC after long-term organic manure application to the red soil of southern China. *European Journal of Soil Science,* 64**,** 797-804.

ZSOLNAY, A. 2001. The prediction of the environmental function of the dissolved organic matter in ecosystems. Final Report of the European Science Foundation Exploratory Workshop.